4.GS:
Rpi 80
2. 2

STATE OF ILLINOIS
DWIGHT H. GREEN, *Governor*
DEPARTMENT OF REGISTRATION AND EDUCATION
FRANK G. THOMPSON, *Director*

DIVISION OF THE
STATE GEOLOGICAL SURVEY
M. M. LEIGHTON, *Chief*
URBANA

REPORT OF INVESTIGATIONS—NO. 80

MODERN CONCEPTS OF CLAY MATERIALS

BY

RALPH E. GRIM

REPRINTED FROM THE JOURNAL OF GEOLOGY,
VOL. L, NO. 3, APRIL-MAY, 1942

ILLINOIS GEOLOGICAL
SURVEY LIBRARY
JUL 30 1975

PRINTED BY AUTHORITY OF THE STATE OF ILLINOIS

URBANA, ILLINOIS
1942

ORGANIZATION

STATE OF ILLINOIS

HON. DWIGHT H. GREEN, *Governor*

DEPARTMENT OF REGISTRATION AND EDUCATION

HON. FRANK G. THOMPSON, *Director*

BOARD OF NATURAL RESOURCES AND CONSERVATION

HON. FRANK G. THOMPSON, *Chairman*
EDSON S. BASTIN, PH.D., D.SC., *Geology*
ROGER ADAMS, PH.D., D.SC., *Chemistry*
LOUIS R. HOWSON, C.E., *Engineering*
WILLIAM TRELEASE, D.SC., LL.D., *Biology*
EZRA JACOB KRAUS, PH.D., D.SC., *Forestry*
ARTHUR CUTTS WILLARD, D.ENGR., LL.D.
President of the University of Illinois

GEOLOGICAL SURVEY DIVISION

M. M. LEIGHTON, *Chief*

ILLINOIS STATE GEOLOGICAL SURVEY
3 3051 00005 7053

SCIENTIFIC AND TECHNICAL STAFF OF THE

STATE GEOLOGICAL SURVEY DIVISION

100 Natural Resources Building, Urbana

M. M. LEIGHTON, PH.D., *Chief*
ENID TOWNLEY, M.S., *Assistant to the Chief*
JANE TITCOMB, M.A., *Geological Assistant*

GEOLOGICAL RESOURCES

Coal

G. H. CADY, PH.D., *Senior Geologist and Head*
L. C. MCCABE, PH.D., *Geologist* (on leave)
R. J. HELFINSTINE, M.S., *Assoc. Mech. Eng.*
JAMES M. SCHOPF, PH.D., *Asst. Geologist*
J. NORMAN PAYNE, PH.D., *Asst. Geologist*
CHARLES C. BOLEY, M.S., *Asst. Mining Eng.*
BRYAN PARKS, M.S., *Asst. Geologist*

Industrial Minerals

J. E. LAMAR, B.S., *Geologist and Head*
H. B. WILLMAN, PH.D., *Assoc. Geologist*
DOUGLAS F. STEVENS, M.E., *Research Associate*
ROBERT M. GROGAN, PH.D., *Asst. Geologist*
ROBERT R. REYNOLDS, B.S., *Research Assistant*

Oil and Gas

A. H. BELL, PH.D., *Geologist and Head*
G. V. COHEE, PH.D., *Asst. Geologist*
FREDERICK SQUIRES, B.S., *Assoc. Petr. Eng.*
CHARLES W. CARTER, PH.D., *Asst. Geologist*
WILLIAM H. EASTON, PH.D., *Asst. Geologist*
PAUL G. LUCKHARDT, M.S., *Research Assistant*
WAYNE F. MEENTS, *Research Assistant*

Areal and Engineering Geology

GEORGE E. EKBLAW, PH.D., *Geologist and Head*
RICHARD F. FISHER, M.S., *Asst. Geologist*

Subsurface Geology

L. E. WORKMAN, M.S., *Geologist and Head*
TRACY GILLETTE, PH.D., *Asst. Geologist*
ARNOLD C. MASON, B.S., *Asst. Geologist*
KENNETH O. EMERY, PH.D., *Asst. Geologist*
MERLYN B. BUHLE, M.S., *Asst. Geologist*
FRANK E. TIPPIE, B.S., *Asst. Geologist*

Stratigraphy and Paleontology

J. MARVIN WELLER, PH.D., *Geologist and Head*
CHALMER L. COOPER, M.S., *Assoc. Geologist*

Petrography

RALPH E. GRIM, PH.D., *Petrographer*
RICHARDS A. ROWLAND, PH.D., *Asst. Petrographer*

Physics

R. J. PIERSOL, PH.D., *Physicist*
B. J. GREENWOOD, B.S., *Mech. Engineer*
DONALD O. HOLLAND, M.S., *Asst. Physicist* (on leave)

GEOCHEMISTRY

FRANK H. REED, PH.D., *Chief Chemist*
H. W. JACKMAN, M.S.E., *Chemical Engineer*
ROBERTA M. LANGENSTEIN, B.S., *Chemical Assistant*
MELVILLE A. ROGERS, B.S., *Research Assistant*

Coal

G. R. YOHE, PH.D., *Assoc. Chemist*
MYRON H. WILT, B.S., *Research Assistant*

Industrial Minerals

J. S. MACHIN, PH.D., *Chemist and Head*
DELBERT L. HANNA, A.M., *Research Assistant*

Fluorspar

G. C. FINGER, PH.D., *Assoc. Chemist*
EVERETT W. MAYNERT, B.S., *Research Assistant*

X-ray and Spectrography

W. F. BRADLEY, PH.D., *Assoc. Chemist*

Analytical

O. W. REES, PH.D., *Chemist and Head*
L. D. MCVICKER, B.S., *Asst. Chemist*
P. W. HENLINE, M.S., *Asst. Chemical Engineer*
WILLIAM F. WAGNER, M.S., *Asst. Chemist*
K. F. BURSACK, B.A., *Research Assistant*
MARION LUND DICKMAN, B.S., *Research Assistant*

MINERAL ECONOMICS

W. H. VOSKUIL, PH.D., *Mineral Economist*
GRACE N. OLIVER, A.B., *Assistant in Mineral Economics*

EDUCATIONAL EXTENSION

DON L. CARROLL, B.S., *Assoc. Geologist*

PUBLICATIONS AND RECORDS

GEORGE E. EKBLAW, PH.D., *Geologic Editor*
CHALMER L. COOPER, M.S., *Geologic Editor*
DOROTHY E. ROSE, B.S., *Technical Editor*
KATHRYN K. DEDMAN, M.A., *Asst. Technical Editor*
ALMA R. SWEENY, A.B., *Technical Files Clerk*
PORTIA ALLYN SMITH, *Asst. Technical Files Clerk*
RUTH E. ROTH, B.S., *Asst. Technical Files Clerk*
MEREDITH M. CALKINS, *Geologic Draftsman*
LESLIE D. VAUGHAN, *Asst. Photographer*
DOLORES THOMAS SIMS, B.A., *Geologic Clerk*

Special Staff to Aid in the War Effort

Oil and Gas Resources

EARLE F. TAYLOR, M.S., *Asst. Geologist*
ARNOLD BROKAW, M.S., *Spec. Asst. Geologist*
M. W. PULLEN, JR., M.S., *Spec. Asst. Geologist*
PAUL K. SIMS, M.S., *Spec. Asst. Geologist*
JOHN A. HARRISON, B.S., *Spec. Research Assistant*

Underground Water Geology

CARL A. BAYS, PH.D., *Spec. Geologist*
C. LELAND HORBERG, PH.D., *Spec. Asst. Geologist*
STEWART FOLK, M.S., *Spec. Asst. Geologist*
ERNEST P. DUBOIS, B.S., *Spec. Asst. Geologist*
ROBERT R. STORM, A.B., *Spec. Asst. Geologist*
PAUL HERBERT, JR., B.S., *Spec. Asst. Geologist*
CHARLES G. JOHNSON, A.B., *Spec. Asst. Geologist*

Consultants: *Ceramics*, CULLEN W. PARMELEE, M.S., D.Sc., and RALPH K. HURSH, B.S., *University of Illinois*
Pleistocene Invertebrate Paleontology, FRANK COLLINS BAKER, B.S., *University of Illinois*
Mechanical Engineering, SEICHI KONZO, M.S., *University of Illinois*.

Topographic Mapping in Cooperation with the United States Geological Survey.

This Report is a Contribution of the Division of Petrography.

March 15, 1942

Digitized by the Internet Archive
in 2012 with funding from
University of Illinois Urbana-Champaign

http://archive.org/details/modernconceptsof80grim

VOLUME L NUMBER 3

THE
JOURNAL OF GEOLOGY

April-May 1942

MODERN CONCEPTS OF CLAY MATERIALS[1]

RALPH E. GRIM
Illinois State Geological Survey

ABSTRACT

Clay materials are composed essentially of minute crystalline particles of any one or more members of a few groups of minerals known as the "clay minerals." Using this clay-mineral concept as a point of departure, researches starting from the many fields in which clay materials are important—from agriculture, engineering, geology, and the ceramic, rubber, paper, petroleum, and many other industries—have in the last fifteen years made outstanding progress toward a more satisfactory and complete understanding of the precise composition of clay materials, their structure, and the factors that determine their properties.

The occurrence of the various clay minerals in soils, contemporaneous sediments, and ancient clays and shales is summarized briefly, and general conclusions are drawn that seem warranted. Pertinent information on the composition, structure, and certain properties of the individual clay minerals is assembled. Finally, the structural relationships of clay-mineral particles and water are analyzed for clay materials in the plastic state, and some new interpretations are suggested.

INTRODUCTION

Clay materials are important in many fields of human endeavor: in agriculture, because they make up an essential part of soils; in construction engineering, because structures are built on them and with them; and in the ceramic, rubber, paper, petroleum, metal-founding, and many other industries, because they are an important raw material. Research workers in all these fields have always been intensely interested in clay materials, and a great fund of information regarding them has gradually accumulated.

[1] Address delivered at the Fiftieth Anniversary Celebration of the University of Chicago, September, 1941.

About fifteen years ago new research tools became available for the investigation of clay materials that opened new fields for fundamental study. As a consequence, new interest was aroused in clay problems, and clay-research activities began an expansion that is still continuing. Mineralogists, physicists, chemists, and engineers from various fields began fundamental studies that have made outstanding progress toward a more satisfactory and complete understanding of the composition, occurrence, and properties of clay materials. This recent work has shown for the first time the character of the mineralogical units that make up clay materials, including their finest size grades. Also, and of great importance, it has shown the lattice structures of these individual units that are the building-blocks of clay materials. An outgrowth of this work has been the so-called "clay-mineral concept" of the composition of clay materials.

Along with the studies of the precise composition of clays has come a tremendous amount of work on the properties of the individual clay minerals, and this work has led to a real insight into the cause of the properties of clay materials and the factors that determine them. In addition, work on the origin and distribution of the clay minerals promises to permit a more satisfactory unraveling of the geologic record locked up in argillaceous sediments.

DEFINITIONS

Although everyone knows what is meant by the term "clay," a precise definition is not easy to formulate. Recently quite satisfactory definitions have been published by the Committee on Sedimentation of the National Research Council[2] and by a committee of the American Ceramic Society,[3] following independent study of present and past usage of this term.

The term "clay" as used today carries with it three implications: (1) a natural material with plastic properties, (2) an essential composition of particles of very fine size grades, and (3) an essential composition of crystalline fragments of minerals that are essentially hydrous aluminum silicates or occasionally hydrous magnesium

[2] W. H. Twenhofel, "Terminology of Fine-grained Mechanical Sediments," *Nat. Res. Coun. Rept. Com. on Sed. 1936–37* (1937), pp. 81–104.

[3] "American Ceramic Society Committee Report," *Bull. Amer. Ceramic Soc.*, Vol. XVIII (1939), pp. 213–15.

silicates. The term implies nothing regarding origin but is based on properties, texture, and composition, which are, of course, interrelated—for example, the plastic properties are the result of the constituent minerals and their small grain size.

"Shale" is the term used generally[4] to designate material that differs from clay only in being laminated and slightly more indurated.

"Clay material" is used in this report to designate any natural material having the three attributes listed previously. It includes, therefore, such material as clay, shales, soils (of the agriculturist), etc. The term "clay material" is preferred as a general term rather than "clay," because the truth is that in many fields some such materials are not thought of as falling under the classification of clay. The term is not used here to include materials composed primarily of bauxitic or limonitic material. These materials may be fine grained, but they do not possess those attributes of composition or properties required by the term "clay."

CONCEPTS OF THE COMPOSITION OF CLAY MATERIALS

Many concepts of the composition of clay materials have been suggested. For a consideration of them the works of J. M. van Bemmeln,[5] H. Stremme,[6] H. E. Ashley,[7] G. Caslow,[8] E. Dittler,[9] H. Salmang,[10] S. Mattson,[11] S. J. Thugutt,[12] J. Lemberg,[13] and R. Gans[14] should be consulted.

[4] Twenhofel, *op. cit.*

[5] "Contribution to the Knowledge of Silicate Disintegration Products in Clayey, Volcanic, and Lateritic Soils," *Zeitschr. anorg. Chem.*, Vol. XLII (1904), pp. 265–314.

[6] "The Chemistry of Kaolins," *Fortschr. Min. Krist. u. Petrog.*, Vol. II (1912).

[7] "Colloid Matter of Clay and Its Measurement," *U.S. Geol. Surv. Bull. 388* (1909), p. 62.

[8] "Relations between Kaolin and Clay," *Chem. d. Erde*, Vol. II (1926), pp. 415–41.

[9] "Chemic-genetic Problems of Clay and Kaolin Research," *Tonindustrie-Zeitung*, Vol. LVI (1932), pp. 836–38, 891–93, 939–40.

[10] *Ceramics* (Berlin, 1933).

[11] "Chemical Characteristics of Soil Profiles," *Lantbrukshogskolans, Annales 2* (Stockholm, Sweden, 1935).

[12] "Are Allophane, Halloysite, Montmorillonite Units or Are They Mixtures of Alumina and Silica Gels," *Centralblatt f. Min.*, 1911, pp. 97–103.

[13] "On the Alteration of Silicates," *Zeitschr. deutsch. geol. Gesellsch.*, Vol. XXVIII (1876), pp. 519–672; "On the Rock Alteration at Predazzo and Monzoni," *ibid.*, Vol. XXIX (1877), pp. 457–511.

[14] "Zeolites and Similar Compounds, Their Constitution and Significance," *Jahrb. kgl. preusz. geol. Landesandst*, Vol. XXVI (1906), p. 179.

With the development of X-ray diffraction analysis a research tool became available for determining the makeup of the finest fraction of clay materials. A. Hadding,[15] in 1923, and F. Rinne,[16] in 1924, were the first to apply this tool to clays. It soon became evident that clays were composed almost entirely of crystalline material and that the properties of clays would have to be explained on the basis of definite crystalline compounds. X-ray researches, materially aided by precise and painstaking optical work by C. S. Ross[17] and others,[18] soon revealed the specific mineral identity of the components of clay materials. As a result of this work the present widely accepted concept of the clay-mineral composition of clay materials was developed.

CLAY-MINERAL CONCEPT

Extensive research[19] in many laboratories has shown, beyond reasonable doubt, that clay materials are composed essentially of crystalline particles of members of any one or more of a few groups of minerals known as the "clay minerals." The clay minerals are hydrous aluminum silicates, frequently with some replacement of the aluminum by iron and magnesium and with small amounts of alkalies and alkali-earths. In rare instances magnesium and iron completely replace the aluminum. In addition to the clay minerals, variable but usually small amounts of quartz, limonitic material,

[15] "An X-ray Method to Identify Crystalline and Cryptocrystalline Substances," *Zeitschr. Krist.*, Vol. LVIII (1923), pp. 108–12.

[16] "X-ray Investigation of Finely Divided Minerals, Manufactured Products and Dense Rocks," *Zeitschr. Krist.*, Vol. LX (1924), pp. 55–69.

[17] "The Mineralogy of Clays," *1st Internat. Cong. Soil Sci.*, Vol. V (1928), pp. 555–56.

[18] C. E. Marshall, "The Orientation of Anisotropic Particles in an Electrical Field," *Trans. Faraday Soc.*, Vol. XXVI (1930), pp. 173–89; R. E. Grim, "Petrography of the Fuller's Earth Deposit, Olmsted, Illinois, with a Brief Study of Some Non-Illinois Earths," *Econ. Geol.*, Vol. XXVIII (1933), pp. 345–63.

[19] S. B. Hendricks and W. H. Frey, "The Results of X-ray and Microscopic Examinations of Soil Colloids," *Soil Sci.*, Vol. XXIX (1930), pp. 457–78; W. P. Kelley, W. H. Dore, and S. M. Brown, "The Nature of the Base-Exchange Material of Bentonite, Soils, and Zeolites as Revealed by Chemical Investigations and X-ray Analysis," *Soil. Sci.*, Vol. XXXI (1931), pp. 25–45; Grim, *op. cit.;* K. Endell, U. Hofmann, and D. Wilm, "The Nature of Ceramic Clays," *Ber. deutsch. keram. Gesellsch.*, Vol. XIV (1933), pp. 407–38; C. W. Correns, "On the Constituents of Clay," *Zeitschr. deutsch. geol. Gesellsch.*, Vol. LXXXV (1933), pp. 706–11; Marshall, "Mineralogical Methods for the Study of Silts and Clays," *Zeitschr. Krist.*, Vol. XC (1935), pp. 8–34.

boehmite, hydrargillite,[20] and organic material may be present. Feldspar, pyrite, and a host of other minerals may be present as extremely minor constituents or as prominent constituents in occasional clays. Except for a few clay minerals—for example, attapulgite—that are fibrous,[21] all the clay minerals occur in flat flake-shaped particles. (See discussion of the structures of the clay minerals.)

The clay minerals occur in most clay materials in particles less than about 5 μ (0.005 mm.) in diameter. They possess excellent cleavages; and, when mixed with water, the particles are frequently reduced in size,[22] so that a wet determination of the particle-size distribution will usually show most of the clay minerals in particles less than 0.002 mm. even though they are coarser in the crude state. Recent studies with the electron microscope[23] have indicated that certain of the clay minerals can exist in particles approaching their unit cell height, that is about 1 mμ. Organic materials may be present in particles less than 0.1 μ in diameter, and the particles of hydroxides of aluminum and ferric iron may be at least as small as 1 μ. Silica in the form of quartz is known[24] in clay materials as small as 0.1 μ, and perhaps in even smaller size grades in the form of cristobalite.[25]

The clay minerals, except allophane,[26] are crystalline; and much

[20] Mehmel, "X-ray Data for Mineral Determinations," *Fortschr. Min. Krist. u. Petrog.*, Vol. XXIII (1939), pp. 91–118.

[21] W. F. Bradley, "The Structural Scheme of Attapulgite," *Amer. Min.*, Vol. XXV (1940), pp. 405–10; G. Nagelschmidt, "Rod-shaped Clay Particles," *Nature*, Vol. CXLII (1938), pp. 114–15.

[22] Grim, "Relation of Composition to Properties of Clays," *Jour. Amer. Ceramic Soc.*, Vol. XXII (1939), pp. 141–51.

[23] M. Ardenne, K. Endell, and U. Hofmann, "Investigation of the Finest Fractions of Bentonite and Clay Soils with the Universal Electron Microscope," *Ber. deutsch. keram. Gesellsch.*, Vol. XXI (1940), pp. 209–27.

[24] Grim and R. H. Bray, "The Mineral Constitution of Various Ceramic Clays," *Jour. Amer. Ceramic. Soc.*, Vol. XIX (1936), pp. 307–15.

[25] A. von Moos, "Unconsolidated Sediments and Soil Mechanics," *Geol. Rund.*, Vol. XXIX (1938), pp. 368–81; Marshall, "Layer Lattices and the Base-Exchange Clays," *Zeitschr. Krist.*, Vol. XCI (1935), pp. 433–49.

[26] C. S. Ross and P. F. Kerr, "Halloysite and Allophane," *U.S. Geol. Surv. Prof. Paper 185-G* (1935).

research[27] indicates that almost all clays, including their smallest constituent particles, are made up entirely of crystalline material. Some clay materials[28] do contain a small amount of amorphous inorganic substance, but it is an extraneous material. The crystalline clay minerals are the dominant components of clay materials, and their properties must be accounted for on the basis of the crystalline components.

FACTORS CONTROLLING THE PROPERTIES OF CLAYS

Following are the factors which are necessary to characterize completely a clay material. These are also the general factors that determine what the properties of a given clay material will be.

1. Clay-mineral composition—the relative abundance of the clay-mineral components and their particle-size distribution.
2. Nonclay-mineral composition—the relative abundance of each mineral and the size-grade distribution of its particles.
3. Electrolyte content—quantitative determinations of the individual exchangeable bases and any water-soluble salts.
4. Organic content—the amount and kind.
5. Miscellaneous textural characteristics[29] such as shape of quartz grains, degree of parallel orientation of the clay-mineral particles, silicification, etc.

Ultimate chemical composition has been omitted from the list of factors controlling properties because it is the units (i.e., minerals) in which the silica, alumina, etc., are combined, rather than their total amounts, that are important. However, if one is interested in a single property, particularly a fired property such as burning color, an ultimate analysis may be of value. It is generally true that a chemical analysis alone, without X-ray, optical, and other mineralogical data, tells very little about the properties of a clay material and, in fact, the analysis may be completely misleading.[30]

[27] Endell *et al.*, *op. cit.;* Grim and Bray, *op. cit.;* K. Jasmund, "Mineral Content of Kaolin with Special Consideration of Colloidal Size Ranges," *Chem. d. Erde.*, Vol. XII (1940), pp. 508–35.

[28] Grim, *op. cit.;* Ross and Kerr, *op. cit.;* Correns, *op. cit.;* H. J. Hellmers and R. Kohlers, "The Determination of Alumina and Silica Gel in Soils by Optical Methods," *Mitt. preuss. geol. Landesanst.*, Vol. XXI (1935).

[29] Grim, "Petrographic and Ceramic Properties of the Pennsylvanian Shales of Illinois," *Jour. Amer. Ceramic Soc.*, Vol. XXIV (1941), pp. 23–28.

[30] Mehmel, "New Methods for the Study of Clays," *Zement, H. 4–6* (1939), 15 pp.; Marshall, "The Chemical Composition and Crystal Structure of the Clay Minerals," *3d Internat. Cong. Soil Sci.*, Vol. III (1936), pp. 95–97.

No mention is made of pH for the reason that the character and relative amount of the ions that determine the pH are important rather than the pH itself.[31] Similarly, no mention is made of base-exchange capacity because that depends on the character of the clay mineral, and for certain clay minerals (see later discussion of base exchange) also on particle size.

CLAY MINERALS—CLASSIFICATION AND COMPOSITION

The clay minerals are the primary constituents of clay materials, and they are the most important single factor in determining the properties of these materials.

GROUPS OF MAJOR IMPORTANCE

Illite group.—The name "illite" was suggested by Grim, Bray, and Bradley[32] as a group name rather than as a specific mineral name for the constituents of clay materials that are similar to, but not identical to, the white micas. Illites contain less potash and more water than the white micas and also differ from them in certain physical properties. The presence of such constituents in clays had been recognized before, and the names "mica-like clay mineral,"[33] "sericite-like mineral,"[34] and "potash-bearing clay mineral"[35] had been applied. These names were confusing, and, as available data suggested that such constituents should be placed together in a single group, a name for the group became desirable.

Grim and others[36] advanced the general formula $(OH)_4K_y(Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)Si_{8-y} \cdot Al_yO_{20}$ with y varying from 1 to 1.5. This

[31] Endell and P. Vageler, "The Cation and Water Hull of Ceramic Clays in the Unfired State," *Ber. deutsch. keram. Gesellsch.*, Vol. XIII (1932), pp. 377–411; R. C. Spivey, "Bentonite in Southwestern South Dakota," *Rept. Invest. 36, So. Dakota Geol. Surv.* (1940).

[32] Grim, Bray, and Bradley, "The Mica in Argillaceous Sediments," *Amer. Min.*, Vol. XXII (1937), pp. 813–29.

[33] Endell, Hofmann, and Maegdefrau, "The Nature of Clay Used as Raw Material in the German Cement Industry," *Zement*, Vol. XXIV (1935), pp. 625–32; Maegdefrau and Hofmann, "The Mica Clay Mineral," *Zeitschr. Krist.*, Vol. XCVIII (1937), pp 31–59.

[34] Grim, "Petrology of the Pennsylvanian Shales and Non-calcareous Underclays of Illinois," *Bull. Amer. Ceramic Soc.*, Vol. XIV (1935), pp. 113–19, 129–34, 170–76.

[35] Ross and Kerr, "The Clay Minerals and Their Identity," *Jour. Sed. Pet.*, Vol. I (1931), pp. 55–65.

[36] Grim, Bray, and Bradley, *op. cit.*

formula indicates that illites may be heptaphyllitic and octophyllitic, which is contrary to A. N. Winchell's[37] finding of "no evidence of crystal solubility between octophyllite and heptaphyllite micas." Recent work by S. B. Hendricks and M. E. Jefferson[38] has tended to support the division of the micas into the two groups suggested by Winchell. Muscovite is heptaphyllitic and so has only two-thirds of the possible positions in the alumina sheet occupied, whereas biotite is octophyllitic and so has all the possible positions filled. (See discussion of structure.) Maegdefrau and Hofmann[39] have shown that illite (the mica-clay mineral) is structurally like muscovite rather than biotite. Most illites that have been analyzed are definite heptaphyllites, but a few contain an excess of iron and/or magnesium. Whether this excess is due to a failure to purify completely the sample or to an actual mixing of types remains to be decided by further work.

Illites are known which contain almost no iron,[40] but most of them contain some replacement of aluminum by iron and magnesium. The upper limit of aluminum replacement is not known. According to Maegdefrau and Hofmann[41] and Hendricks and L. T. Alexander,[42] glauconite is closely similar in structure to the illites.

Montmorillonite group.—This group takes its name from the mineral montmorillonite, with a probable composition of $(OH)_4Al_4Si_8O_{20} \cdot xH_2O$.[43] The aluminum is usually partly replaced by magnesium and ferric iron. In some cases the substitution is essentially complete, and then the names "saponite" and "nontronite" are applied, respectively. All the members of this group have an expanding lattice (see discussion of structure of the clay minerals), and this has come to be the diagnostic criterion for this group. Beidellite has been placed in this group and defined as differing from montmorillonite by having a molecular silicate-to-alumina ratio of 3:1 instead

[37] "Studies in the Mica Group," *Amer. Jour. Sci.*, ser. 5, Vol. IX (1925), pp. 309–27, 415–30.

[38] "Polymorphism of the Micas," *Amer. Min.*, Vol. XXIV (1939), pp. 729–71.

[39] *Op. cit.* [40] *Ibid.* [41] *Ibid.*

[42] "Minerals Present in Soil Colloids," *Soil Sci.*, Vol. XLVIII (1939), pp. 257–71.

[43] U. Hofmann, K. Endell, and D. Wilm, "Crystal Structure and Swelling of Montmorillonite," *Zeitschr. Krist.*, Vol. LXXXVI (1933), pp. 340–48.

of 4:1.[44] Unpublished work by the writer and his colleagues indicates that some so-called "beidellite" is a mixture of montmorillonite and limonite and that some others have a nonexpanding lattice which, together with other properties, suggests that they are clay-mineral mixtures containing large amounts of illite. The validity of the species is, therefore, open to question.

Kaolinite group.—Kaolinite, the chief member of this group, has the composition $(OH)_8Al_4Si_4O_{10}$.[45] Dickite and nacrite, with the same composition but slightly different crystallographic forms, are very rare constituents of argillaceous sediments. Anauxite, like kaolinite except for a higher silica-to-alumina molecular ratio, is also a member of this group. Only a few occurrences of anauxite have been reported.[46]

Constituents of clays have been reported that could be interpreted as kaolinite in which the aluminum has been replaced by ferric iron;[47] however, stronger evidence favors the conclusion that such substitution does not actually exist. Hendricks[48] has recently pointed out structural reasons for the absence of substitutions in the kaolinite lattice.

GROUPS OF MINOR IMPORTANCE

Halloysite.—Hofmann, Endell, and Wilm[49] stated that halloysite with the composition $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ ($[OH]_{16} \cdot Al_4 \cdot Si_4 \cdot O_6$) loses $2H_2O$ on heating to about 50° C. and changes over to kaolinite. Mehmel[50] has confirmed the change of 50° C. but has shown that the

[44] Ross and Kerr, *op. cit.*

[45] Ross and Kerr, "The Kaolin Minerals," *U.S. Geol. Surv. Prof. Paper 165-E* (1931).

[46] V. T. Allen, "Eocene Anauxite Clays and Sands in the Coast Range of California," *Bull. Geol. Soc. Amer.*, Vol. LII (1941), pp. 271–94.

[47] J. S. Hosking, "The Soil Clay Mineralogy of Some Australian Soils Developed on Basaltic and Granitic Parent Material," *Jour. Coun. Sci. and Ind. Res.*, Vol. XIII (1941), pp. 206–11.

[48] "Random Structures of Layer Minerals as Illustrated by Cronstedite ($2FeO \cdot Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$). Possible Iron Content of Kaolinite," *Amer. Min.*, Vol. XXIV (1939), pp. 529–39.

[49] "X-ray and Colloid Chemical Study of Clays," *Zeitschr. angewandte Chemie*, Vol. XLVII (1934), pp. 539–47.

[50] "On the Structure of Halloysite and Metahalloysite," *Zeitschr. Krist.*, Vol. XC (1935), pp. 35–43.

mineral resulting after the loss of $2H_2O$ is not kaolinite. Accordingly, there are two forms of halloysite, which Mehmel designates as "halloysite," $(OH)_{16}Al_4 \cdot Si_4O_6$, and "metahalloysite," $(OH)_8Al_4Si_4O_{10}$, the latter being the higher temperature form. Hendricks[51] has suggested the names "hydrated halloysite" and "halloysite," respectively, for these minerals, thus retaining the name "halloysite" for material of the composition to which it was first applied. In recent work C. H. Edelman and J. Ch. L. Favejee[52] have followed the usage of Mehmel because "the name 'hydrated halloysite' for the mineral rich in water gives the erroneous impression that this substance originates from the mineral poor in water." Actually, the higher hydrated form has not been prepared from the lower hydrated form in the laboratory. No substitutions within the lattice of the halloysite minerals have been reported.

Attapulgite.[53]—The name "attapulgite" was suggested by J. de Lapparent[54] for the unique clay mineral composing certain Georgia and Florida fuller's earths and clays at Mormoiron, France. Recent work of Bradley[55] tends to confirm the species, and he suggests the formula $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$ in which there is some replacement of Mg by Al. De Lapparent[56] gives $Si_3O_{12}(Al_{4/3} \cdot Mg_2)H_8$ as the formula for the mineral.

Allophane.—Ross and Kerr[57] suggest that the term "allophane" be used to include all noncrystalline mutual solutions of silica, alumina, and water in varying amounts. Minor amounts of bases may also be present. The term "allophane" would then be applicable to the small amount of amorphous material found occasionally in some clays.

[51] "On the Structure of the Clay Minerals, Dickite, Halloysite, and Hydrated Halloysite," *Amer. Min.*, Vol. XXIII (1938), pp. 275–301.

[52] "On the Crystal Structure of Montmorillonite and Halloysite," *Zeitschr. Krist.*, Vol. CII (1940), pp. 417–31.

[53] Unfortunately not named "Floridin," since the fuller's earth that contains it in Georgia and Florida was known first by that name.

[54] "An Essential Constituent of Fuller's Earth," *Compt. rend. Acad. sci.*, Vol. CCI (1935), pp. 481–83.

[55] "The Structural Scheme of Attapulgite," *Amer. Min.*, Vol. XXV (1940), pp. 405–10.

[56] "Formula and Structural Scheme of Attapulgite," *Compt. rend. Acad. sci.*, Vol. CCII (1936), pp. 1728–31.

[57] *Op. cit.*

The term "allophane" or "allophaneton"[58] has been used widely in Europe, particularly by ceramists, to designate the portion of a clay that is soluble in hydrochloric acid. Allophane (usage of Ross and Kerr) and the montmorillonite minerals are more acid-soluble than the other clay minerals, but the use of allophane based on acid solubility has no mineralogical significance,[59] chiefly because the effect of variations in particle size is ignored.

Chloritic mica.—Microscopic study of clays and shales composed largely of illite frequently shows green flaky masses of material that have the optical properties of chloritic micas. X-ray diffraction analyses of the finer fractions of such rocks also indicate the presence of crystalline material with the general characteristics of chloritic mica. It has not yet been possible to isolate this material so that it could be studied in detail and definitely classified.

QUESTIONABLE CLAY MINERALS

Fersman[60] suggested the existence of a series of minerals between paramontmorillonite and parasepiolite which he called "palygorskites." Paramontmorillonite and parasepiolite were considered to be acicular forms of montmorillonite and sepiolite. The xylotile group was considered to contain the iron analogues of the palygorskites. According to De Lapparent,[61] thermal analyses indicate that palygorskites are mixtures of kaolinite and sepiolite. H. Longchambon[62] and P. Urbain[63] have also discussed the palygorskites.

According to Ross and Kerr,[64] the type "leverrierite" is composed

[58] H. Stremme, "The Clay Minerals," *Sprechsaal*, Vol. XLVII (1914); Thugutt, *op. cit.*

[59] H. S. Washington, "The Calculation of the 'Rational Analysis' of Clays," *Jour. Amer. Ceramic Soc.*, Vol. I (1918), pp. 405–21; J. S. McDowell, "Rational Analysis of Clay," *Jour. Amer. Ceramic Soc.*, Vol. XIX (1926), pp. 61–65.

[60] A. Fersman, "On the Palygorskite Group," *Bull. Acad. Imp. Sci. St. Petersburg*, Vol. II (1908), pp. 255–74.

[61] "The Place of Montmorillonite in the Group of Phyllite Silicates," *Compt. rend. Acad. sci.*, Vol. CCI (1935), pp. 527–29.

[62] "Characteristics of Palygorskites," *Compt. rend. Acad. sci.*, Vol. CCIV (1937), pp. 55–58.

[63] "Classification of Hydrated Aluminum Silicates," *Compt. rend. Soc. geol. de France*, 1936, pp. 147–49.

[64] *Op. cit.*

of kaolinite, whereas, according to De Lapparent,[65] the name refers to a mixture of white mica and kaolinite. In any event, the term does not designate a single species and should be abandoned.

Kerr[66] has shown that the type "smectite" is composed of montmorillonite. Faratsihite, according to Hendricks,[67] is a mixture of nontronite and kaolinite.

The exact status of other suggested species, such as monothermite,[68] keffekillite,[69] gedroizite,[70] bravaisite, elbrussite,[71] ablykite,[72] and donbassite,[73] remains for future work to decide.

It should not be assumed that all valid species of clay minerals have been described. Particularly in the case of the magnesium-clay minerals, it seems possible that other species will be found. There are some clays, such as the bentonite from Tehachapi, California, that contain appreciable magnesium (8 per cent $\pm$MgO),[74] and their properties do not seem to fit exactly with described species. W. von Englehardt,[75] De Lapparent,[76] and D. P. Serdyuchenko[77]

[65] "Constitution and Origin of Leverrierite," *Compt. rend. Acad. sci.*, Vol. CXCVIII (1934), pp. 669–71.

[66] "Montmorillonite or Smectite as Constituents of Fuller's Earth and Bentonite," *Amer. Min.*, Vol. XVII (1932), pp. 192–97.

[67] "Random Structures . . . . ," *op. cit.*

[68] D. S. Beliankin, "On the Characteristics of the Mineral 'Monothermite,'" *Compt. rend. Acad. sci. U.S.S.R.*, Vol. XVIII (1938), pp. 673–76.

[69] Anonymous, "Deposits of 'Kel'-like Clays in the Tertiary Formations of the Crimea," *United Geol. and Prosp. Serv. U.S.S.R. Bull. 50* (1930), pp. 1131–40.

[70] I. D. Sedletsky, "Gedroizite in the Alkali-Soils," *Compt rend. Acad. sci. U.S.S.R.*, Vol. XXIII (1939), pp. 565–68.

[71] I. J. Mickey, "On a New Mineral of the Nontronite-Beidellite Group," *Centralblatt f. Min.*, Vol. A (1930), pp. 293–303.

[72] Sedletsky and S. Yusupova, "Argillaceous Minerals Closely Approaching Halloysite," *Compt. rend. Acad. sci. U.S.S.R.*, Vol. XXVI (1940), pp. 944–47.

[73] E. K. Lazarenko, "Donbassites, a New Group of Minerals from the Donetz Basin," *Compt. rend. Acad. sci. (Doklady) U.S.S.R.*, Vol. XXVIII (1940), pp. 509–21.

[74] Kerr and E. M. Cameron, "Fuller's Earth of Bentonite Origin from Tehachapi, California," *Amer. Min.*, Vol. XXI (1936), pp. 230–37.

[75] "The Silicate Clay Minerals," *Fortschr. Min. Krist. u. Petrog.*, Vol. XXI (1937), pp. 276–337.

[76] "Formulae, Structures, and Classification of Clays," *Zeitschr. Krist.*, Vol. XCVIII (1938), pp. 233–58.

[77] "About the Constitution and Nomenclature of Some Water Aluminum Silicates," *17th Internat. Geol. Cong. Spec. Pub. No. 10* (1937).

have recently discussed in detail the problems of these magnesium-clay minerals.

INTERSTRATIFIED CLAY MINERALS

Recent investigations have shown that when several clay-mineral species are present in a clay material they are often closely intergrown. The intergrowth is essentially an interstratification of basal cleavage plates of the different clay minerals. Hendricks and Alexander[78] have indicated an interstratification of montmorillonite and illite in the colloid fractions of certain soils, and Bray[79] has made the same suggestion for some Illinois soils. Hendricks[80] has shown that faratsihite is an intergrowth of kaolinite and nontronite, and De Lapparent[81] uses the term "leverrierite" to indicate a mixture of white mica and kaolinite.

Unpublished work by the author and Bradley has checked the conclusions of Hendricks and Bray for soil colloids. The general character of the optical properties of such intergrowths in some soils would seem to require a regular, rather than a random, intergrowing with the units of the different clay minerals of the order of height of about one unit cell. It has been observed frequently that many shales containing kaolinite, chloritic micas, and illite probably represent less-intimate intergrowth than in the soil colloids.

The existence of such intergrowths vastly complicates the complete identification of all the clay minerals in a given clay material. Frequently the use of a single criterion for identification of the constituent minerals will not reveal all the components of the interstratification. Only a combination of optical, X-ray, chemical, and thermal data will provide the complete picture.

CLAY MINERALS—STRUCTURE

Since the application of X-ray diffraction analysis to clay minerals, a vast body of data has accumulated on the lattice structure of these minerals. The details of some of these structures are still a matter of some controversy, but the broader features based on gen-

[78] *Op. cit.*

[79] "Chemical and Physical Changes in Soil Colloids with Advancing Development in Illinois Soils," *Soil Sci.*, Vol. XLIII (1937), pp. 1–14.

[80] "Random Structures . . . . ," *op. cit.*

[81] "Constitution and Origin . . . . ," *op. cit.*, pp. 669–710.

eralizations of L. Pauling[82] seem to be reasonably well established. For the details of the individual structures the cited references should be consulted.

Two structural units are involved in the atomic lattices of the clay minerals. One is the alumina or aluminum hydroxide unit, which consists of two sheets of closely packed oxygens or hydroxyls between which aluminum atoms are embedded in such a position that they are equidistant from six oxygens or hydroxyls. Actually, only two-thirds of the possible aluminum positions are occupied in this unit, which is the gibbsite structure. The mineral brucite possesses a similar structure except that all possible aluminum positions are occupied by magnesium. The second unit consists of a sheet of tetrahedral silica (SiO_4) groups linked to form a hexagonal network of the composition Si_4O_{10} when repeated indefinitely. This unit may be viewed as a sheet of loosely packed oxygen atoms with each oxygen linked to two silicon atoms directly beneath. The silicon atoms are in tetrahedral positions, three valences being satisfied by linkage to three oxygens in the overlying sheet. The fourth silicon valency is satisfied below by an oxygen atom such that that silicon valency is analogous to the common hydroxyl group of gibbsite.

Montmorillonite.—The montmorillonite structure suggested by Hofmann, Endell, and Wilm[83] consists of structural units of one gibbsite sheet between two sheets of silica tetrahedral groups (Fig. 1). The structural units are stacked one above the other in the direction of the *c*-axis and, according to Maegdefrau and Hofmann,[84] without orientation in the *a* and *b* directions. Hendricks and Ross,[85] however, on the basis of optical and diffraction data, indicate some orientation in the *a* and *b* directions.

The units are loosely held together in the direction of the *c*-axis

[82] "The Structure of Micas and Related Minerals," *Proc. Nat. Acad. Sci.*, Vol. XVI (1930), pp. 123–29.

[83] *Op. cit.*

[84] "The Crystal Structure of Montmorillonite," *Zeitschr. Krist.*, Vol. XCVIII (1937), pp. 299–323.

[85] "Lattice Limitations of Montmorillonite," *Zeitschr. Krist.*, Vol. C (1938), pp. 251–64.

with water present between them. The amount of water between the units varies, and there is a correlated variation in the *c*-dimension, so that the mineral is said to have an expanding lattice. Without water between the structural units the lattice is like that of pyrophyllite except that the height of the cell is 9.6 A, as against 9.2 A for pyrophyllite. The increased height of the montmorillonite cell is explained[86] by the presence of cations between the units. In the absence of water the distance between the units measured from the

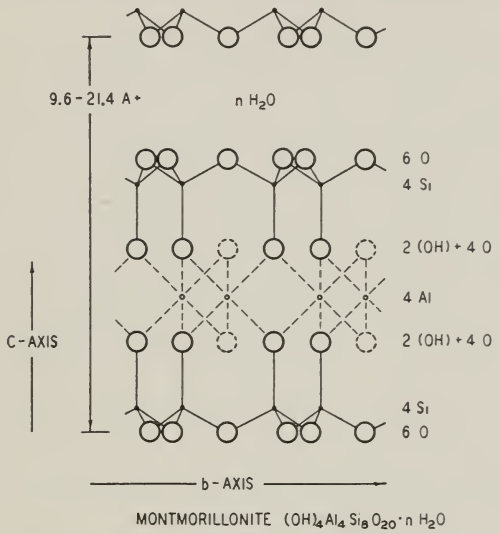

FIG. 1.—Schematic presentation of the structure of montmorillonite. (After Hofmann, Endell, and Wilm.)

centers of oxygens is 3.0 A. According to Hofmann and J. Endell,[87] the maximum recorded expansion has given a *c*-dimension of 30 A. Maegdefrau and Hofmann[88] state that the mineral is orthorhombic, whereas Gruner[89] believes it to be monoclinic.

Replacement of Al^{+++} gibbsite positions by Mg^{++} and Fe^{+++} lead

[86] "The Relation of Cation Exchange and Swelling of Montmorillonite to Preheating," *Zeitschr. verien. deutsch. Chem.*, Vol. XXXV (1939).

[87] *Ibid.*

[88] "The Crystal Structure . . . . ," *op. cit.*

[89] "The Structural Relationships of Nontronite and Montmorillonite," *Amer. Min.* Vol. XX (1935), pp. 475–83.

eralizations of L. Pauling[82] seem to be reasonably well established. For the details of the individual structures the cited references should be consulted.

Two structural units are involved in the atomic lattices of the clay minerals. One is the alumina or aluminum hydroxide unit, which consists of two sheets of closely packed oxygens or hydroxyls between which aluminum atoms are embedded in such a position that they are equidistant from six oxygens or hydroxyls. Actually, only two-thirds of the possible aluminum positions are occupied in this unit, which is the gibbsite structure. The mineral brucite possesses a similar structure except that all possible aluminum positions are occupied by magnesium. The second unit consists of a sheet of tetrahedral silica (SiO_4) groups linked to form a hexagonal network of the composition Si_4O_{10} when repeated indefinitely. This unit may be viewed as a sheet of loosely packed oxygen atoms with each oxygen linked to two silicon atoms directly beneath. The silicon atoms are in tetrahedral positions, three valences being satisfied by linkage to three oxygens in the overlying sheet. The fourth silicon valency is satisfied below by an oxygen atom such that that silicon valency is analogous to the common hydroxyl group of gibbsite.

Montmorillonite.—The montmorillonite structure suggested by Hofmann, Endell, and Wilm[83] consists of structural units of one gibbsite sheet between two sheets of silica tetrahedral groups (Fig. 1). The structural units are stacked one above the other in the direction of the *c*-axis and, according to Maegdefrau and Hofmann,[84] without orientation in the *a* and *b* directions. Hendricks and Ross,[85] however, on the basis of optical and diffraction data, indicate some orientation in the *a* and *b* directions.

The units are loosely held together in the direction of the *c*-axis

[82] "The Structure of Micas and Related Minerals," *Proc. Nat. Acad. Sci.*, Vol. XVI (1930), pp. 123–29.

[83] *Op. cit.*

[84] "The Crystal Structure of Montmorillonite," *Zeitschr. Krist.*, Vol. XCVIII (1937), pp. 299–323.

[85] "Lattice Limitations of Montmorillonite," *Zeitschr. Krist.*, Vol. C (1938), pp. 251–64.

with water present between them. The amount of water between the units varies, and there is a correlated variation in the *c*-dimension, so that the mineral is said to have an expanding lattice. Without water between the structural units the lattice is like that of pyrophyllite except that the height of the cell is 9.6 A, as against 9.2 A for pyrophyllite. The increased height of the montmorillonite cell is explained[86] by the presence of cations between the units. In the absence of water the distance between the units measured from the

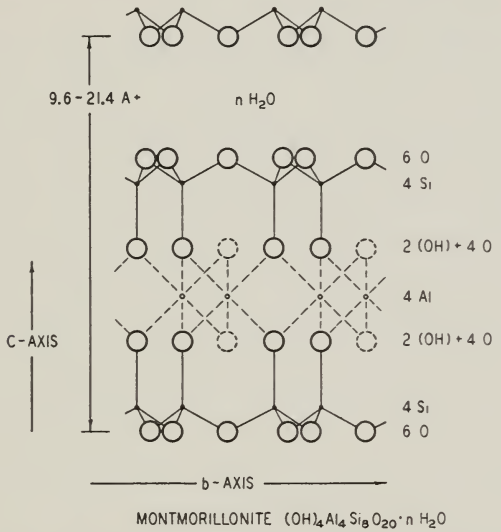

FIG. 1.—Schematic presentation of the structure of montmorillonite. (After Hofmann, Endell, and Wilm.)

centers of oxygens is 3.0 A. According to Hofmann and J. Endell,[87] the maximum recorded expansion has given a *c*-dimension of 30 A. Maegdefrau and Hofmann[88] state that the mineral is orthorhombic, whereas Gruner[89] believes it to be monoclinic.

Replacement of Al^{+++} gibbsite positions by Mg^{++} and Fe^{+++} lead

[86] "The Relation of Cation Exchange and Swelling of Montmorillonite to Preheating," *Zeitschr. verien. deutsch. Chem.*, Vol. XXXV (1939).

[87] *Ibid.*

[88] "The Crystal Structure . . . . ," *op. cit.*

[89] "The Structural Relationships of Nontronite and Montmorillonite," *Amer. Min.* Vol. XX (1935), pp. 475–83.

to saponite and nontronite, respectively. It has been suggested[90] that Si^{++++} may be replaced by Al^{+++}, and Marshall[91] believes that beidellite is the member of the montmorillonite group in which such replacement has been appreciable. G. Nagelschmidt[92] believes that about 1 out of 6 Si^{++++} may be replaceable by Al^{+++}. Substitution of Al^{+++} for Si^{++++} to a marked degree leads to the nonexpanding muscovite structure and therefore appears unlikely,[93] unless it is assumed that the charges resulting from the substitution are balanced in the alumina sheet.[94]

A striking property of the montmorillonite lattice is that aluminum can be removed by acid leaching until there is only 1.7 Al to 4 Si before the lattice structure is destroyed.[95] The aluminum is removed first to exchange positions before going into solution. Leaching with salt solution also removes some aluminum from the lattice.[96]

The amount of the expansion of the montmorillonite lattice is related to the character of the exchangeable base carried by the mineral.[97] For example, Hofmann and K. Giese[98] have suggested that Ca-montmorillonite swells more than NH_4-montmorillonite, and Hofmann and Bilke[99] have shown that montmorillonite with either Na^+, Ca^{++}, or H^+ swells about the same small amount at low vapor pressures but that at higher vapor pressures Na-montmorillo-

[90] Hofmann and W. Bilke, "On the Inner Crystalline Swelling and Base Exchange Capacity of Montmorillonite," *Kolloid Zeitschr.*, Vol. LXXVII (1936), pp. 238–51; Marshall, "Layer Lattices . . . . ," *op. cit.*

[91] Marshall, "Layer Lattices . . . . ," *op. cit.*

[92] "On the Atomic Arrangement and Variability of the Members of the Montmorillonite Group," *Min. Mag.*, Vol. XXV (1938), pp. 140–55.

[93] Grim, "Properties of Clays," *Recent Marine Sediments* (Tulsa, Okla.: Amer. Assoc. Pet. Geol., 1939).

[94] Hofmann and Bilke, *op. cit.*

[95] *Ibid.*

[96] Marshall, "Layer Lattices . . . . ," *op. cit.*

[97] C. W. Davis, H. C. Vacher, and J. E. Conley, "Bentonite, Its Properties, Mining, Preparation and Utilization," *U.S. Bur. of Mines Tech. Paper 609* (1940); H. Freundlich, B. Schmidt, and G. Landau, "The Thixotropy of Bentonite Suspensions," *Kolloid Beihefte*, Vol. XXXVI (1932), pp. 43–81.

[98] "On the Base-Exchange of Clay Minerals," *Kolloid Zeistschr.*, Vol. LXXXVII (1939), pp. 21–36.

[99] Hofmann and Bilke, *op. cit.*

nites swell much more than the others. In general, it appears that Li^+ and Na^+ favor great swelling, whereas Ca^{++}, Mg^{++}, Al^{+++}, H^+, Fe^{+++}, and K^+ tend to reduce it.

The structural unit $Al_4Si_8O_{20}(OH)_4$ suggested by Hofmann and others[100] is a balanced unit and does not explain satisfactorily the swelling in the presence of water, the high base-exchange capacity, and the large adsorption between the basal planes. (See later discussion of base exchange.) Primarily for these reasons, this structural scheme has been questioned by W. Bragg,[101] A. D. Garrison,[102] J. Holzner,[103] De Lapparent,[104] and Edelman and Favejee.[105]

Holzner[106] suggests the formula $Al_{2.3}Si_4O_{10}(OH)_3$ and a structure consisting of a pile of $Al_2(OH)_6$ and a hypothetical unit $Al_{2/3}Si_2O_5$. There appears to be no real basis for such a structure, and it has met with no approval. De Lapparent[107] has suggested a structure that is essentially a combination of pyrophyllite layers and brucite layers $Mg_3(OH)_6$ in which Si has been substituted for 2Mg. This structure has also met with no approval since its thickness is greater than the (001) spacing determined by X-ray analysis.

Recently Edelman and Favejee[108] have suggested a structure that differs from Hofmann's structure[109] in having every other tetrahedron of the silica sheet inverted (Fig. 2) and the substitution of (OH) for the O positions that, as a consequence, would not be balanced. In other words, the silica sheet is considered to have the configuration of cristobalite. According to this scheme, the formula of the silica sheet becomes $O_2Si_4O_6(OH)_2$; of the whole mineral, $(OH)_{12}Al_4Si_8O_{16}\cdot nH_2O$. The mineral should therefore contain $3H_2O$ per Al_2O_3 when $n=0$. It is claimed that this structure more satisfactorily ex-

[100] Hofmann, Endell, and Wilm, *op. cit.*

[101] "Clay," *Royal Inst. Great Britain*, November 19, 1937.

[102] "Surface Chemistry of Clays and Shales," *Amer. Inst. Min. and Met. Engineers, Tech. Pub. 1027* (1938).

[103] "Preliminary Discussion of the Chemical Composition of the Clay Minerals and Corresponding Silicates of Trivalent and Bivalent Metals," *Chem. d. Erde*, Vol. IX (1935), pp. 464–85.

[104] "Formulae, Structures . . . . ," *op. cit.* [105] *Op. cit.* [106] *Op. cit.*

[107] "Formulae, Structures . . . ," *op. cit.*

[108] *Op. cit.* [109] Hofmann, Endell, and Wilm, *op. cit.*

plains certain physical properties of montmorillonite and the differences between it and pyrophyllite.

W. F. Bradley, R. E. Grim, and G. L. Clark[110] presented evidence to show that the swelling of montmorillonite may take place step-

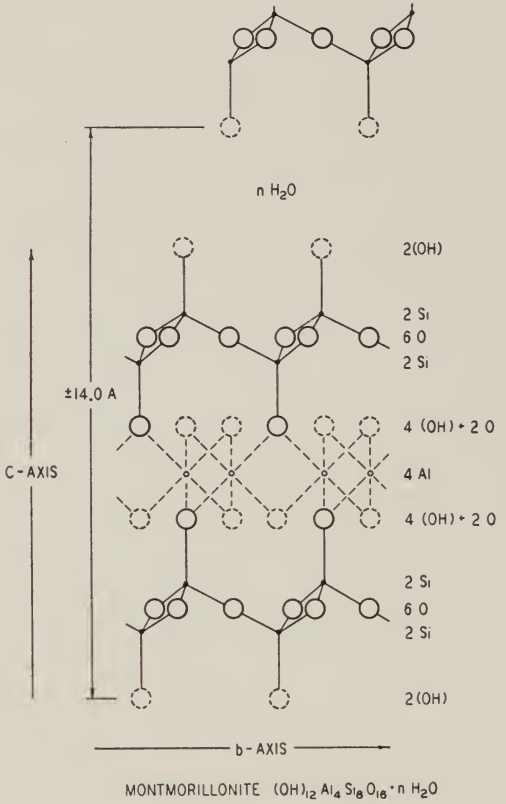

FIG. 2.—Schematic presentation of the structure of montmorillonite. (After Edelman and Favejee.)

wise by the formation of discrete hydrates. According to them, the successive hydrates have *c*-dimensions of 9.6 A, 12.4 A, 15.4 A, 18.4 A, and 21.4 A, corresponding to $2H_2O$, $8H_2O$, $14H_2O$, $20H_2O$, and $26H_2O$. Nagelschmidt[111] has reached a different conclusion. Ac-

[110] "A Study of the Behavior of Montmorillonite upon Wetting," *Zeitschr. Krist.*, Vol. XCVII (1937), pp. 216–22.

[111] "On the Lattice Shrinkage and Structure of Montmorillonite," *Zeitschr. Krist.*, Vol. XCIII (1936), pp. 481–87.

cording to him, as the H_2O increases from 0 to 4 per unit cell, (001) expands from 10.5 A to 15 A; from 4 to 10 H_2O, (001) expands from 15 to 15.9 A; from 10 to 15 H_2O there is no significant expansion; and from 15 to 20 H_2O, (001) expands markedly to 19 A. Maegdefrau and Hofmann[112] conclude that the swelling is continuous. All these workers considered that the water molecules were close packed in the sheets between the basal planes. Very recently Hendricks and others[113] have presented evidence to indicate that the water molecules are not densely packed. (See p. 271 for discussion of configuration of water molecules in the sheets.) According to these workers, the usual situation is that the cleavage spacing varies continuously but not uniformly with the water content. They interpret this as a result of an averaging effect from a lattice that contains various numbers of water layers in different parts. On this interpretation the discrete hydration states referred to above[114] would actually be $2H_2O$, $6H_2O$, $10H_2O$, etc., and these very probably were the states observed.

Illite.—The illite structure is similar to that of montmorillonite suggested by Hofmann and others[115] except that about 15 per cent of the Si^{++++} positions are replaced by Al^{+++}, and the resulting excess charges are satisfied chiefly by K^+ ions between the silica sheets of two successive units[116] (Fig. 3). The K^+ ions appear to act as bridges binding the units together so that they do not expand in the presence of water. The illite structure is similar to the structure of muscovite suggested by Pauling[117] and confirmed by W. Jackson and J. West[118] except that in muscovite one-fourth of the Si^{++++} positions are occupied by Al^{+++} and the number of K^+ is proportionately greater.

In illite Mg^{++} and Fe^{+++} can be substituted for Al^{+++} in the

[112] "The Crystal Structure . . . . ," *op. cit.*

[113] "Hydration Mechanism of the Clay Mineral Montmorillonite Saturated with Various Cations," *Jour. Amer. Chem. Soc.*, Vol. LXII (1940), pp. 1457–64.

[114] Bradley, Grim, and Clark, *op. cit.*

[115] Hofman, Endell, and Wilm, *op. cit.*

[116] Grim, Bray, and Bradley, *op. cit.*

[117] *Op. cit.*

[118] "The Crystal Structure of Muscovite," *Zeitschr. Krist.*, Vol. LXXVI (1930), pp. 211–27.

octahedral sheet. There appears to be some doubt that Mg^{++} can occupy all the possible positions, that is, substitutions of $3Mg^{++}$ for $2Al^{+++}$, although further work is necessary to settle this point. In other words, illite appears to be heptaphyllitic rather than octophyllitic and to be structurally similar to muscovite rather than to biotite.[119] According to Maegdefrau and Hofmann,[120] the substitution of Mg^{++} for Al^{+++} can be compensated for by substitution of

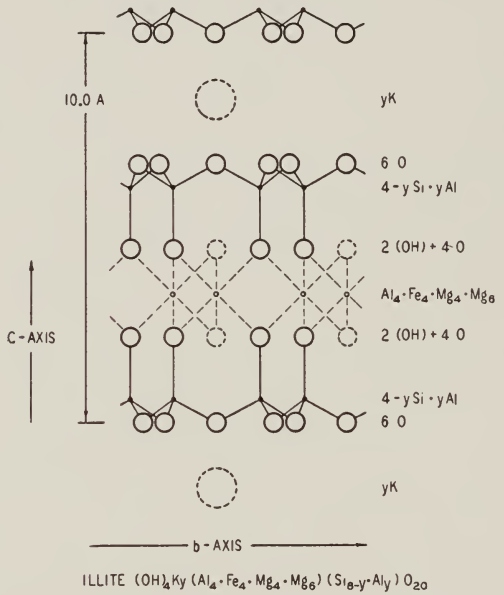

FIG. 3.—Schematic presentation of the crystal structure of illite. (After Grim, Bray, and Bradley.)

(OH) for O, thereby partly explaining the higher water content in illite than in muscovite.

Maegdefrau and Hofmann[121] believe that the diffraction data can be interpreted as an orthorhombic structure, whereas most other workers[122] favor a monoclinic structure. Illite has a pronounced basal cleavage, but it is not so easily cleavable as montmorillonite.

[119] Maegdefrau and Hofmann, "The Mica Clay . . . . ," *op. cit.;* Hendricks and Jefferson, *op. cit.*

[120] Maegdefrau and Hofmann, "The Mica Clay . . . . ," *op. cit.*

[121] *Ibid.*

[122] Hendricks and Jefferson, *op. cit.*

Kaolinite.—The kaolinite structure, as worked out by Gruner,[123] is composed of a gibbsite sheet with a single tetrahedral silica sheet (Fig. 4). The lattice structure does not expand with varying water content, probably because of the attraction of O and (OH) layers which are adjacent when kaolinite units are stacked one above the other. The mineral has basal cleavage but is distinctly less cleavable than montmorillonite. No replacements of the aluminum by iron or magnesium have been proved.

To account for the higher silica-to-alumina molecular ratio of the anauxite member of this group, it was suggested[124] that Si^{++++} replaces Al^{+++}. A recent, more favored suggestion[125] is that some Al^{+++} positions are vacant with corollary changes of O and (OH) to balance the charges on the lattice.

The structures of dickite[126] and nacrite[127] differ from that of kaolinite primarily by a shift or rotation of the layers as they are placed one above the other. According to Gruner,[128] the structure of the kaolinite minerals is monoclinic.

Halloysite.—According to Mehmel,[129] halloysite (hydrated halloysite of Hendricks) is made up of an alternating succession of $Si_2O_3(OH)_2$ and $Al_2(OH)_6$ sheets in the *c*-axis direction (Fig. 5). These sheets are not tied to each other by mutual oxygens. Metahalloysite (halloysite of Hendricks) forms from halloysite by the joining-together of the alumina and silica sheets with the condensation of 2(OH) to form H_2O, which escapes, and O, which forms a

[123] "The Crystal Structure of Kaolinite," *Zeitschr. Krist.*, Vol. LXXXIII (1932), pp. 75–88.

[124] *Ibid.;* Gruner, "Densities and Structural Relationships of Kaolinites and Anauxites," *Amer. Min.*, Vol. XXII (1937), pp. 855–60.

[125] Hendricks, "Concerning the Crystal Structure of Kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and the Composition of Anauxite," *Zeitschr. Krist.*, Vol. XCV (1936), pp. 245–52.

[126] Gruner, "The Crystal Structure of Dickite," *Zeitschr. Krist.*, Vol. LXXXIII (1932), pp. 394–404.

[127] Gruner, "The Crystal Structure of Nacrite and a Comparison of Certain Optical Properties of the Kaolin Group with Its Structure," *Zeitschr. Krist.*, Vol. LXXXV (1933), pp. 345–54; Hendricks, "The Crystal Structure of Nacrite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and the Polymorphism of the Kaolin Minerals," *Zeitschr. Krist.*, Vol. C (1938), pp. 509–18.

[128] "The Crystal Structure of Nacrite . . . . ," *op. cit.*

[129] "On the Structure of Halloysite . . . . ," *op. cit.*

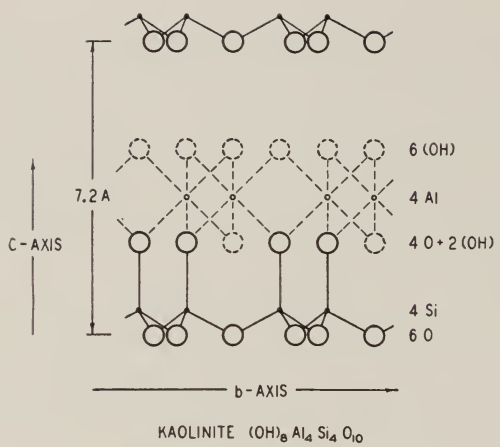

FIG. 4.—Schematic presentation of the crystal structure of kaolinite. (After Gruner)

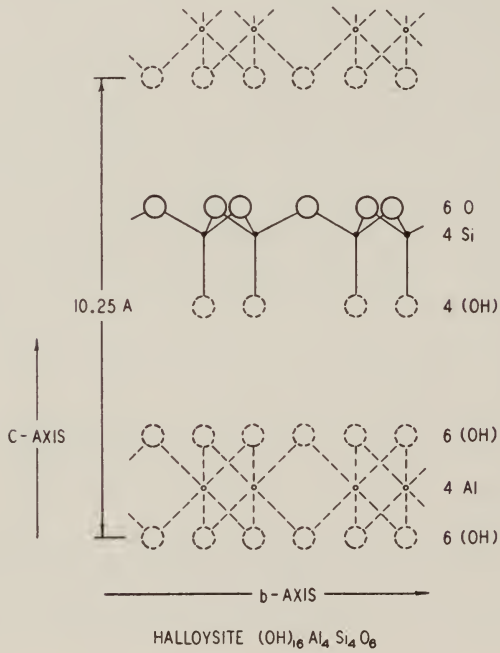

FIG. 5.—Schematic presentation of the crystal structure of halloysite. (After Mehmel.)

bond between the sheets. The resulting structure is closely similar to that of kaolinite.

Hendricks[130] objected to Mehmel's structures because the interaction of the hydroxyl groups would seem to require considerable energy and thus a higher temperature than 50° C. and because the observed intensities of certain reflections are not in accord with expected values. Hendricks[131] suggested that halloysite is composed of neutral ($OH_4Si_2Al_2O_5$) layers interleaved with layers of ($2H_2O$) molecules. Hendricks and M. E. Jefferson[132] explain the limitation of the water molecules to a single layer as due to the O and (OH) sheets of successive layers being adjacent and the resulting partial bonding of the water through (OH) ions.

On the basis of general studies of the properties of the halloysite minerals, P. P. Stout[133] and Edelman and Favejee[134] have suggested other structural arrangements. The former investigator, on the basis of phosphate-fixation experiments, suggested that the halloysite cell consists of two kaolinite layers having their (OH) ion sheets adjacent.

Edelman and Favejee[135] have objected to all the suggested structures on the basis that there is no satisfactory way in which the sheets of the hydrated form are kept together. However, the suggestion of Hendricks and others[136] of an orientation of the water molecules in the sheet (see p. 264) may serve as an explanation. Edelman and Favejee[137] suggest a structure in which every other silica tetrahedron is inverted with substitutions of (OH) for O to balance the charges (Fig. 6). The formula of the unit would be $Al_2(OH)_5OSi_2O_3(OH)$ or $Al_2O_3 \cdot 2SiO_2 \cdot 3H_2O$. According to this arrangement, the additional H_2O necessary to fulfil the formula of $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ exists free between the basal sheets. The change to metahalloysite

[130] "On the Structure of the Clay . . . . ," *op. cit.*

[131] *Ibid.*

[132] "Structure of Kaolin and Talc-Pyrophyllite Hydrates and Their Bearing on Water Sorption of Clays," *Amer. Min.*, Vol. XXIII (1933), pp. 863–75.

[133] "Alterations in the Crystal Structure of Clay Minerals as a Result of Phosphate Fixation," *Proc. Soil Sci. Soc. Amer.*, Vol. IV (1939), pp. 177–82.

[134] *Op. cit.*

[135] *Ibid.*

[136] "Structure of Kaolin . . . . ," *op. cit.* [137] *Op. cit.*

takes place by the loss of the H_2O between the basal planes and the action of the (OH) of the silica sheet with an (OH) of the adjacent $Al_2(OH)_6$ sheet of the next unit to form H_2O and a joint O. As evidence for this structure, it is suggested that it explains the similarity of the adsorptive properties of the mineral to those of montmorillonite. It should be pointed out that there is little agreement among students of clay as to the precise character of the adsorptive properties of the halloysite minerals.

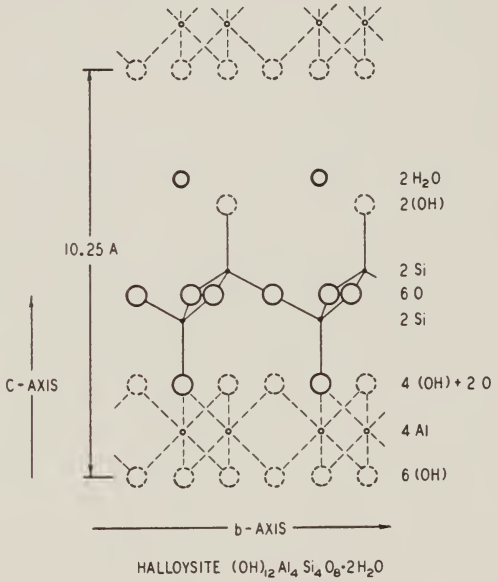

FIG. 6.—Schematic presentation of the crystal structure of halloysite. (After Edelman and Favejee.)

Careful optical work with halloysite shows certain peculiarities difficult to explain on the basis of the suggested structures. If suspensions of halloysite are allowed to dry slowly in a flat-bottomed vessel, so that aggregates are formed,[138] some of them show very perfect interference figures, indicating definite crystal orientation of the units in the aggregate, whereas others appear to be entirely amorphous. All other clay minerals under similar conditions yield aggregates that always show the crystalline character of the min-

[138] Grim, "The Petrographic Study of Clay Minerals—a Laboratory Note," *Jour. Sed. Pet.*, Vol. IV (1934), pp. 45–47.

erals. It would seem from these data that halloysite is composed of units that may easily vary from definite alignment to a random orientation.

Attapulgite.—De Lapparent[139] has suggested that attapulgite is a layer silicate related to the micas. Bradley[140] has shown, however, that the X-ray diagrams obtained for the mineral are "fiber dia-

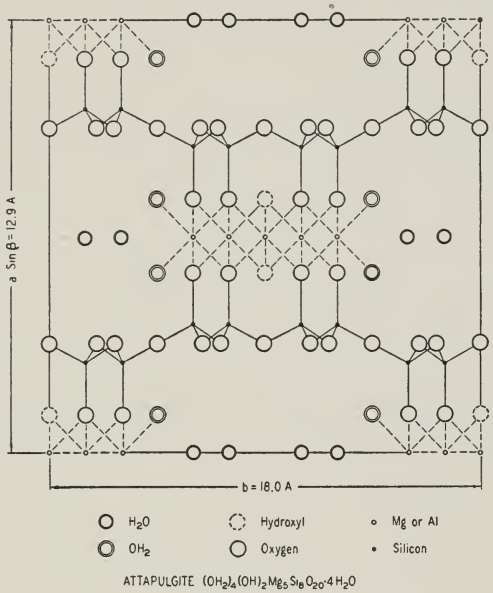

FIG. 7.—Schematic presentation of the crystal structure of attapulgite. (After Bradley.)

grams." The structure suggested by Bradley (Fig. 7) may be described as units of two silica tetrahedra with a brucite sheet between extending indefinitely in only one direction (instead of two directions, as required by sheets) to form ribbons arranged with their long axes parallel to the *c*-axis. The ribbons are joined together through oxygen bonds of the silica sheets so that the silica sheets viewed above are continuous. Chains of water molecules exist in interstices between the ribbons. The composition of the ideal cell is $(OH_2)_4(OH)_2Mg_5Si_8O_{20}\cdot 4H_2O$. Al^{+++} can replace Mg^{++} accom-

[139] "Formula and Structural . . . . ," *op. cit.* [140] *Op. cit.*

panied by vacancies in octahedral positions or may replace Si^{++++} to a limited extent.

Chlorite.—R. E. McMurchy[141] found the structure of six varieties of chlorite of varying composition to be the same. The units of the structure are alternating mica and brucite sheets, with the ideal formula $Al_2Mg_5Si_3O_{10}(OH)_8$. The size of the unit cell varies slightly in different chlorites, and this is explained by replacement of Mg^{++} by Fe^{++}.

CLAY MINERALS—BASE EXCHANGE[142]

Clay materials have the property of carrying cations that can be exchanged for other cations by treatment with a water solution containing the second cation. In the process the structure of the clay material is not changed. This property of base exchange was first observed in soils by H. S. Thompson[143] in 1845 and was studied by J. T. Way[144] about 1850. It may be a property of both the inorganic and organic components of clay materials, but only that of the inorganic portion is considered herein. It is well known that the fertility and tilth of soils and the physical properties of clay materials generally are closely related to the character of the exchangeable base that they contain.

BASE-EXCHANGE CAPACITY

The property of clay materials to carry exchangeable cations is designated as "base-exchange capacity" and is measured in terms of milliequivalents per 100 gm. (1 m.e. $Na_2O = 0.031$ gm.; 10 m.e. per 100 gm. = 0.31 per cent Na_2O). Numerous methods have been suggested for determining base-exchange capacity, but none of them give results of very high accuracy (± 2 m.e. in 70 m.e.). For a detailed discussion of the various methods the works of Hofmann

[141] "The Crystal Structure of the Chlorite Minerals," *Zeitschr. Krist.*, Vol. LXXXVIII (1934), pp. 420–32.

[142] Clay materials also may carry exchangeable anions, but almost nothing specific is known of this property.

[143] "On the Absorbent Power of the Soil," *Jour. Roy. Agric. Soc.*, Vol. XI (1850), p. 68.

[144] "On the Power of Soils To Absorb Manure," *Jour. Roy. Agric. Soc.*, Vol. XI (1850), p. 13.

and Giese,[145] C. du Rietz,[146] Endell and Vageler,[147] and A. N. Puri and H. L. Uppal[148] should be consulted. Of particular significance in the determination of base-exchange capacity is the fact[149] that free aluminum and ferric iron in a clay tend to clog exchange positions and to reduce the base-exchange capacity, and also that extended acid leaching or salt treatment tends to remove aluminum and ferric iron from the lattice to exchange positions,[150] with a resulting reduction in base-exchange capacity.

Methods for the quantitative determination of the specific exchangeable cations yield results of even lower accuracy than the determinations of total exchange capacity, primarily because of the difficulty of separating the easily soluble salts that clay materials may

TABLE 1

BASE-EXCHANGE CAPACITY

(In Milliequivalents per 100 Gm.)

Montmorillonite	60–100	Kaolinite	3–15
Attapulgite	25– 30	Halloysite*	6–10
Illite	20– 40		

* Edelman, in "Relation between the Crystal Structure of Minerals and Their Base-Exchange Capacity," *3d Internat. Cong. Soil Sci.*, Vol. III (1936), pp. 97–99, has published higher values for halloysite; and it must be concluded that the capacity of the mineral is open to some question.

contain. R. P. Graham and J. Sullivan,[151] Hofmann and Giese,[152] and Endell and Vageler[153] have critically discussed present methods.

In Table 1 values for the base-exchange capacity of the common

[145] *Op. cit.*

[146] *The Base-Exchange Properties of Solid Materials* (Stockholm: printed by author, 1938).

[147] *Op. cit.*

[148] "Critical Examination of the Methods of Finding the Base-Exchange Capacity of Soils," *Soil Sci.*, Vol. XLVII (1939), pp. 245–53.

[149] O. C. Magistad, "The Action of Aluminum, Ferrous and Ferric Iron and Manganese in Base Exchange Reactions," *Arizona Agric. Exper. Sta. Tech. Bull. 18* (1928); Endell, Fendius, and Hofmann, "Base-Exchange Characteristics of Clay and Problems of Moldability in Ceramics," *Ber. deutsch. keram. Gesellsch.*, Vol. XV (1934), pp. 595–625.

[150] A. Brammall and J. G. C. Leech, "Base-Exchange and Its Problems," *Sci. Jour. Roy. College Sci.*, Vol. VIII (1938), pp. 43–51.

[151] "Critical Study of Methods of Determining Exchangeable Bases in Clay," *Jour. Amer. Ceramic Soc.*, Vol. XXI (1938), pp. 176–83.

[152] *Op. cit.* [153] *Op. cit.*

clay minerals are given. The spread of values results from the facts that all the members in a single group do not have exactly the same capacity and that for certain clay minerals the capacity varies with particle size.

RELATION TO PARTICLE SIZE

E. A. Hauser and C. E. Reed[154] have pointed out that the base-exchange capacity of montmorillonite does not vary with its particle size, whereas C. G. Harman and F. Fraulini[155] and S. Spiel[156] have shown that the capacity of kaolinite increases with decreasing particle size. These findings are in accord with differences in the structural characteristics of the minerals and the cause of their adsorptive capacity, to be discussed presently. On the same basis it would be expected that the base-exchange capacity of illite would increase with decreasing particle size. W. P. Kelley and H. Jenny[157] report an increase in the exchange capacity of kaolinite, the micas, and montmorillonite by extremely fine grinding. P. Schachtschabel[158] has failed to check this work. Again on the basis of structure, grinding of kaolinite and mica should increase the base-exchange capacity, but an increase for montmorillonite is difficult to understand.

CAUSE OF ADSORPTIVE PROPERTIES OF CLAY MINERALS

Recent work[159] has shown that about 80 per cent of the exchange positions of montmorillonite are on the basal-plane surfaces and that the remainder are on the edges of the flakes. Hendricks[160] has com-

[154] "The Thixotropic Behavior and Structure of Bentonite," *Jour. Phys. Chem.*, Vol. XLI (1937), pp. 911–34.

[155] "Properties of Kaolinite as a Function of Its Particle Size," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 252–58.

[156] "Effect of Adsorbed Electrolytes on Properties of Monodispersed Clay-Water Systems," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 33–38.

[157] "The Relation of Crystal Structure to Base-Exchange in Soils," *Soil Sci.*, Vol. XLI (1936), pp. 367–81.

[158] "Investigation of the Sorption of Clay Minerals and Organic Soil Colloids, and the Determination of the Proportions of These Colloids in Soils by Sorption Methods," *Kolloid-Beihefte*, Vol. LI (1940), pp. 199–276.

[159] Hendricks, Nelson, and Alexander, *op. cit.*

[160] "Base-Exchange of the Clay Mineral Montmorillonite for Organic Cations and Its Dependence upon Adsorption Due to van der Waal's Forces," *Jour. Phys. Chem.*, Vol. XLV (1940), pp. 65–81.

puted that the area per exchange position for one montmorillonite is about 70 A^2. Oxygens with incompletely satisfied valence bonds must exist at the broken edges of flakes, and these have been considered adequate[161] to hold exchangeable cations. Replacement of the hydrogen[162] of hydroxyls exposed at flake edges has also been suggested to account for some of the capacity.

The basal planes of montmorillonite on the Hofmann structure[163] are made up of oxygens that are balanced, and the explanation for holding cations on these planes is not so obvious. It has been suggested that within the lattice[164] substitutions of Mg^{++} for Al^{+++} and of Al^{+++} for Si^{++++} would provide the charge necessary to hold cations. Grim[165] has indicated that substitutions of Al^{+++} for Si^{++++} provide a lattice similar to that of mica which does not expand, probably because the source of the charge is close to the flake surface. Substitution of Mg^{++} for Al^{+++} is considered a more likely explanation because the source of the charge is farther from the surface and, therefore, is adequate to hold a cation but not to prevent the lattice from expanding. A study of analytical data indicates a relation between substitutions in the alumina sheet and base-exchange capacity for some montmorillonite, but for other montmorillonites[166] apparently there is no such relationship. Hofmann and Bilke[167] have suggested that substitution of Al^{+++} for Si^{++++} may be partly balanced by adjustments in the gibbsite sheet, presumably the remainder of the balancing being done by exchangeable cations. On this basis it may be possible to have substitutions in the silica sheet without the development of the mica lattice.

Lattice substitution undoubtedly plays a part in the base-exchange capacity of montmorillonites, but it seems doubtful that it is the entire explanation for the planar exchange capacity, as it

[161] Endell and Vageler, *op. cit.* [162] Kelley and Jenny, *op. cit.*

[163] Hofmann, Endell, and Wilm, *op. cit.*

[164] Hofmann and Bilke, *op. cit.;* Nagelschmidt, "On the Atomic . . . . ," *op. cit.;* Marshall, "Layer Lattices . . . . ," *op. cit.*

[165] "Properties of Clays," *op. cit.*

[166] W. P. Kelley, A. O. Woodford, W. H. Dore, and S. M. Brown, "The Colloid Constituents of California Soils," *Soil Sci.*, Vol. XLVIII (1939), pp. 201–55.

[167] *Op. cit.*

must be if the Hofmann[168] structure is correct. Edelman and Favejee[169] have emphasized this point and consider their structure as explaining more satisfactorily the exchange capacity of montmorillonite. The basal planes of their structure contain (OH) ions which provide hydrogens for replacement by cations.

The generally low base-exchange capacity of kaolinite suggests that the seat of the normal capacity is limited to broken oxygen bonds and/or the hydrogen of hydroxyls at flake edges. Speil[170] has reached a similar conclusion because of the marked change in base-exchange capacity at pH_7. From another point of view, the exchange capacity of kaolinite is low, because there are no replacements within the lattice to set up unbalanced charges and because the mineral does not break down to thin sheets (see later discussion), and hence comparatively few basal plane (OH) ions are exposed for replacement of hydrogen by a cation. Stout's work[171] indicates that certain ions (phosphate) particularly replace the hydrogen of the (OH) ions and effect replacement between the basal planes. For these ions kaolinite has a very high exchange capacity, and when they are present the unit sheets have a random arrangement. Endell and others[172] consider some of the exchange capacity of extremely fine-grained kaolinites to result from lattice distortion.

Similarly, the seat of much of the capacity of illite is at flake edges. However, there are substitutions in the illite lattice which may provide the charge to hold additional cations. Most illite does not break down very readily into extremely small flakes, so that many of the cations held between basal planes because of lattice replacements would not be replaceable. That some of these interplanar cations are replaceable is suggested by the long period of time necessary for illite to reach equilibrium in base-exchange reactions.[173]

CATION REPLACEABILITY

The relative ease of replacement of one cation by another has been the object of much study, and the following series[174] has been

[168] Hofmann, Endell, and Wilm, *op. cit.*
[169] *Op. cit.*
[170] *Op. cit.*
[171] *Op. cit.*
[172] Endell, Hofmann, and Wilm, *op. cit.*
[173] Schachtschabel, *op. cit.*
[174] E. Hauser, *Colloidal Phenomena* (New York: McGraw Hill Book Co., 1939).

widely accepted: $Li^+ > Na^+ > \ldots > K^+ > Rb^+ > Cs^+ > Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++} > H^+$. Thus, at equivalent concentrations Ca^{++} will displace a greater fraction of Li^+ than K^+. The divalent ions are more tightly held than the monovalent ones, and J. B. Page[175] has recently provided data to emphasize that ion size is important also in replaceability. According to his data, ions of a size permitting them to fit closely into the cavities inside of the hexagonal net of oxygens are least replaceable; for example, K^+ with a diameter of 2.66 A closely fits the cavity which has a diameter of 2.8 A and is tightly held. Also, it follows from this line of reasoning that the cations are held at the clay-mineral surface rather than at some distance from it, as required by Jenny's[176] concept or by the double-layer idea.[177] According to some advocates of the latter idea, the cations are separated from the clay-mineral particles by an inner layer of (OH) ions. From a structural standpoint this does not seem tenable, since the charges on the lattice are mainly such that positive charges would be required to satisfy them. However, as Kelley and Jenny[178] point out, there are cogent chemical reasons why intermediate (OH) ions should exist if the cation is not exchanged for hydrogen of an (OH) of the lattice itself.

G. Wiegner[179] and many others have attributed the replaceability of cations to differences in the degree of their hydration—the most highly hydrated being held loosest, perhaps, because the hydration hull prevented close contact between the cation and the clay-mineral particle.

Later, in discussing the clay-water system in detail, it will be pointed out that some cations (e.g., Na^+), previously thought to be highly hydrated, probably do not hydrate at all and that other cations hydrate to a lesser degree than has been assumed. Cation exchangeability, therefore, cannot be explained satisfactorily on the basis of cation hydration.

[175] "The Relation of Ionic Size to the Fixation of Potassium and Other Cations by Colloidal Clay" (Ph.D thesis, Ohio State University, 1940).

[176] "Studies on the Mechanism of Ionic Exchange in Colloidal Aluminum Silicates," *Jour. Phys. Chem.*, Vol. XXXVI (1932), pp. 2217–58.

[177] H. Freundlich, *Kapillarchemie* (4th ed.; Leipzig, 1930), Vol. I. [178] *Op. cit.*

[179] "Some Physico-Chemical Properties of Clays," *Jour. Soc. Chem. Ind.*, Vol. L (1931), pp. 65–71, 103–12.

A. L. S. Bar and H. J. C. Tenderloo[180] suggested that cation exchangeability should not be the same for all the clay minerals; and Schachtschabel[181] has recently carefully investigated this point, using known pure clay minerals, and has shown definitely that the relative exchangeability is not the same for all the clay minerals. He shows, for example, that for NH_4-montmorillonite H^+ and K^+ are about equally exchangeable, all the univalent ions, except Rb^+ and Cs^+, are more exchangeable than the divalent ions, and all the divalent ions have about the same exchangeability (Fig. 8). For NH_4-kaolinite (Fig. 9) the exchangeability of the cations is about the same as for NH_4-montmorillonite. NH_4^+, however, is more tightly held by kaolinite. For NH_4-muscovite (Fig. 10) H^+ and K^+ are more tightly held than the divalent ions, and NH_4^+ is even more tightly held than in kaolinite. When a mixture of montmorillonite and muscovite is treated with mixtures of calcium and ammonium acetate, the mica adsorbs relatively much more of the NH_4^+, and the montmorillonite adsorbs relatively more of the Ca^{++}. Hendricks[182] has found that Schachtschabel's results for NH_4^+ and Ca^{++} acceptance by mica and montmorillonite do not hold in all details for all samples of these minerals. He has shown that in mica-montmorillonite mixtures the mica preferentially adsorbs H^+ and the montmorillonite Ce^{+++}.

This recent work shows that the exchangeability series given previously does not hold exactly for the individual clay minerals. Actually there is a series for each clay mineral. Schachtschabel[183] is probably correct in his explanation that the phenomenon results from the difference in the size of the cations in relation to the lattice configurations that give rise to base-exchange (broken bonds, substitutions of Al^{+++} by Mg^{++}, etc.). These findings of Schachtschabel[184] illustrate the great necessity of carrying out clay re-

[180] "On the Double Layer of Clay Colloids," *Kolloid-Beihefte*, Vol. XLVII (1936), pp. 97–124.

[181] *Op. cit.*

[182] Hendricks and Alexander, "Semiquantitative Estimation of Montmorillonite in Clays," *Proc. Soil Sci. Soc. of Amer.*, Vol. V (1940), pp. 95–99.

[183] *Op. cit.* [184] *Ibid.*

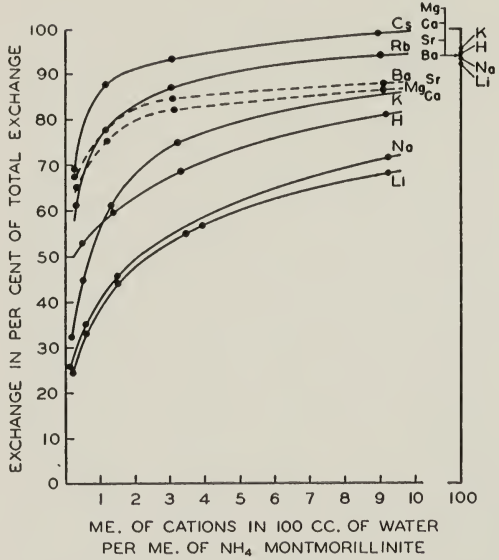

FIG. 8.—NH_4-montmorillonite; ionic exchange with alkali and alkali-earth chlorides. (After Schachtschabel).

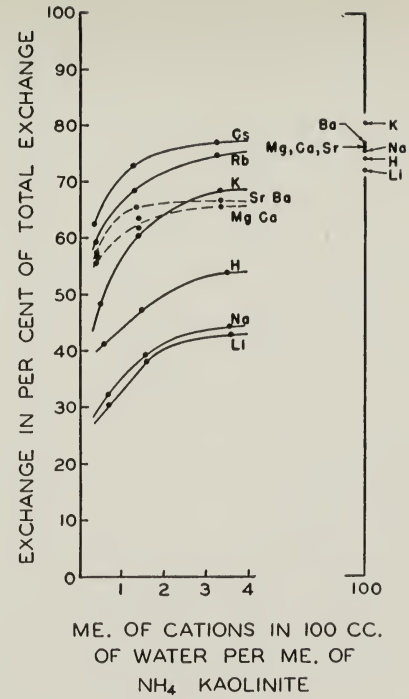

FIG. 9.—NH_4-kaolinite; ionic exchange with alkali and alkali-earth chlorides.(After Schachtschabel.)

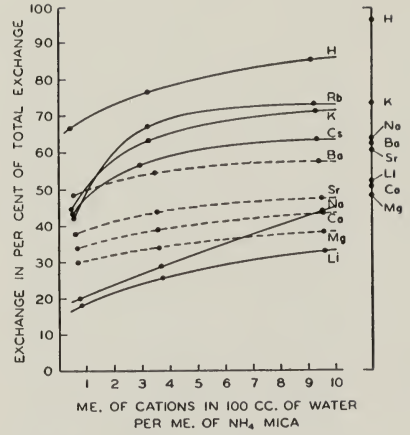

FIG. 10.—NH_4-mica; ionic exchange with alkali and alkali-earth chlorides.(After Schachtschabel.)

searches on material of known clay-mineral composition. Much base-exchange and other chemical work on clays has little value because there is no information on the mineral composition of the material studied.

Recent work by J. E. Gieseking[185] and later by Hendricks[186] has shown that montmorillonite has base-exchange capacity for some large organic cations as well as for inorganic cations. The large organic cations are held between the unit cells in basal planes and practically destroy the swelling of the lattice in the presence of water. The organic cations may be held more firmly than H^+.

CLAY MINERALS—OCCURRENCE

Much data on the composition of various types of argillaceous materials have been published in recent years. No attempt is made to assemble all these data here, but rather to give references to the more important and to deduce from them such general conclusions as appear warranted.

SOILS

Kelley,[187] Hendricks,[188] Bray,[189] and their colleagues in this country, Edelman[190] and his students in Holland and the Dutch East Indies, Hosking[191] and J. Shearer and W. F. Cole[192] in Australasia, C. W. Correns[193] and his students in Germany, and Nagelschmidt

[185] "Mechanism of Cation Exchange in the Montmorillonite-Beidellite-Nontronite Type of Clay Minerals," *Soil Sci.*, Vol. XLVII (1939), pp. 1–14.

[186] "Base Exchange of the . . . . ," *op. cit.*

[187] Kelley *et al.*, "Comparative Study of the Colloid of a Cecil and Susquehanna Profile," *Soil Sci.*, Vol. XLVII (1939), pp. 175–93; "The Colloid Constituents . . . . ," *op. cit.*

[188] Hendricks and Alexander, *op. cit.;* Hendricks and Frey, *op. cit.*

[189] *Op. cit.*

[190] "General Discussions of the Mineralogical Composition of Clays and Qualitative X-ray Analysis of Some Dutch Clays," *Overdruk uit Meded. v. d. Landbouwk.*, Vol. XLIII (1939), pp. 1–39; H. J. Hardon and J. Ch. L. Favejee, "Qualitative X-ray Analysis of the Principal Soil Types of Java," *Overdruk uit Meded. v. d. Landbouwk.*, Vol. XLIII (1939), pp. 1–5.

[191] *Op. cit.*

[192] "X-ray Analysis of Some Tasmanian Soil Colloids," *Jour. Roy. Soc. Western Australia*, Vol. XXVI (1940), pp. 133–37.

[193] "Mineralogical Study of Three Mecklenburg Soils," *Zeitschr. f. Pflanzenern. u. Dungung. u. Bodenk.*, Vol. XLIV (1936), pp. 316–26.

and others[194] in England have led the way in the study of the clay-mineral composition of soils. This work has not yet reached the point of a clear correlation of clay-mineral composition and soil classification based on physical factors or of a precise correlation of environmental factors of soil formation and resulting clay minerals.

Kaolinite, illite, montmorillonite, and halloysite have all been reported in soils, but there is some question regarding the identification of halloysite. It would appear from published data that the halloysite minerals are rare constituents of soils generally. This is not certain, because it is difficult to distinguish between kaolinite and the low hydration form of halloysite.

It is likely that illite is formed infrequently in soils, whereas kaolinite and montmorillonite are commonly formed by soil-forming processes. Illite is present in many soils, but usually as a remnant of the composition of the parent-rock. Kaolinite and montmorillonite may form from the same parent-rock[195] under different environmental conditions. Hosking[196] has shown that in Australia, under conditions of abundant rainfall and active leaching, kaolinite soils form on basic igneous rocks, whereas under conditions of low rainfall and poor leaching montmorillonite soils form from the same igneous rocks.

Some soils contain mixtures of clay minerals, but in many soils there is a single clay mineral that is the dominant component. These are primarily mature soils in which there has been time for the clay mineral to develop, that is, in equilibrium with the environmental factors under which the soil has formed.

Montmorillonitic and kaolinitic soils[197] may form from illitic material, and kaolinitic soils may form from montmorillonite parent-material.[198] As far as the writer is aware, there is no unquestioned example of a montmorillonite soil that has developed from a kaolinite parent-material.

[194] "The Minerals in the Clay Fraction of a Black Cotton Soil and a Red Earth from Hyderabad, Deccan State, India," *Jour. Agric. Sci.*, Vol. XXX (1940).

[195] Nagelschmidt *et al.*, *op. cit.* [196] *Op. cit.*

[197] R. H. Bray, R. E. Grim, W. F. Bradley, and M. M. Leighton, "The Weathering of Loess in Illinois" (unpublished manuscript).

[198] Kelley *et al.*, "Comparative Study of the Colloid . . . . ," *op. cit.*

CONTEMPORANEOUS SEDIMENTS

The work of C. W. Correns,[199] R. Revelle,[200] R. S. Dietz,[201] and Grim and Dietz[202] has made a start in bringing to light the clay-mineral composition of sediments accumulating at the present time on the ocean floors. There appears to be a complete absence of similar data for sediments accumulating today in other environments. Until information regarding these sediments is available, the cycle of changes that argillaceous materials may go through from their source to the site of their accumulation and in later lithification cannot be worked out.

Work to date suggests that illite is the most widely distributed clay mineral in present-day marine argillaceous sediments, that kaolinite is also widely distributed but generally less abundant than illite, and that montmorillonite is usually either absent or of very minor abundance. Dietz[203] suggests that illite is forming in the marine environment of accumulation, perhaps chiefly from montmorillonite. Correns[204] has, however, concluded that there is little transformation of clay minerals on the sea floor.

ANCIENT SEDIMENTS

Sedimentary clays are most frequently mixtures of illite and kaolinite. Occasionally a small amount of montmorillonite is also present, and some of them seem to contain a little halloysite. The Pennsylvanian underclays of Illinois[205] and the Cretaceous and Tertiary clays of the coastal plains are illustrative of the composi-

[199] "Sedimentation in the Deep Sea," *Wissenschaftliche Ergebn. deutsch Atlantischen Expedition auf dem Forschungs u. Vermessungschiff "Meteor,"* Vol. III, Part 3 (Berlin, 1937).

[200] Scripps Inst. of Oceanography, unpublished work. University of California, La Jolla, California.

[201] "Clay Minerals in Recent Marine Sediments" (Ph.D. thesis, University of Illinois, 1941).

[202] "Mineral Composition of Clays from the Floor of the Pacific Ocean off the Coast of California" (unpublished work).

[203] *Op. cit.*

[204] "On the Question of the Formation of Mica in Recent Sediments," *Geol. Rund.*, Vol. XXXIX (1938), pp. 202–22.

[205] Grim and V. T. Allen, "Petrology of the Pennsylvanian Underclays of Illinois," *Bull. Geol. Soc. Amer.*, Vol. XLIX (1938), pp. 1485–1514.

tion of many sedimentary clays. In some clays kaolinite is dominant, in some others illite is most abundant; but usually they are both present in fair abundance. There are some occurrences of sedimentary clays in which other clay minerals are dominant—for example, the Eocene Porter's Creek clay of the Gulf Coast area, containing montmorillonite,[206] and the fuller's earth in the Miocene Hawthorne formation of Georgia and Florida, composed of attapulgite.

In most of the shales that have been studied[207] illite is the dominant clay mineral, and there is some reason to believe that the shaly structure is related to the presence of illite.

The argillaceous material of till and loess, so far as is known, is composed of a mixture of illite, kaolinite, and montmorillonite, with illite the more abundant.

MISCELLANEOUS ARGILLACEOUS MATERIALS

The occurrence of kaolinite minerals in deposits resulting from the action of sulphate waters and of hydrothermal processes has been reviewed by Ross and Kerr.[208] An occurrence of hydrothermal halloysite material has recently been recorded by G. A. Schroter and Ian Campbell.[209] Montmorillonite has also been reported in deposits that are believed to be of hydrothermal origin.[210]

Residual deposits of kaolinite, the precise origin of which has been the subject of much controversy,[211] are widespread and the source of much commercial kaolin. Some of the kaolins are bauxitic in the sense that they contain appreciable amounts of hydrated alumina—for example, boehmite and hydrargillite.

Many bentonite clays formed by the alteration of volcanic ash are

[206] Grim, "Petrography of the Fuller's . . . . ," *op. cit.*

[207] Grim, "Petrographic and Ceramic . . . . ," *op. cit.*

[208] "The Kaolin Minerals," *op. cit.*

[209] "Geologic Features of Some Deposits of Bleaching Clay," *A.I.M.E. Pub. 1139* (1938).

[210] E. Dittler and F. Kirnbauer, "Bentonite at Tomesti, Rumania," *Zeitschr. prakt. Geol.*, Vol. XLI (1933), pp. 121–27; De Lapparent, "Origin of Bentonites from North Africa," *Compt. rend. Soc. geol. de France*, No. 10 (1937), pp. 126–28.

[211] Ross and Kerr, "The Kaolin Minerals," *op. cit.*

composed of montmorillonite clay minerals.[212] Some bentonites also contain cristobalite,[213] and a very small amount of zeolite has also been reported in them.[214]

CLAY MINERALS—REDUCTION OF PARTICLE SIZE ON AGITATION IN WATER

Grim[215] has shown that when clay-mineral particles are agitated in water they tend to break up into smaller-sized units. Because of lattice characteristics, montmorillonite breaks down more readily than kaolinite. Some illites break down easily, whereas others do not. Study of a large number of clays has shown that montmorillonite and some illite minerals readily break down in a suspension into particles less than 0.1 μ in diameter. Kaolinite and most illite minerals are broken down, with difficulty, or not at all, to particles of 1 to 0.1 μ in diameter.

Clearly, in making mechanical analyses of clays the measurements made of particle size represent the degree of disaggregation, and frequently nothing else. Analyses, to be comparable at all, must be made with the same preliminary treatment, including the use of the same electrolyte. Even then, some variation is to be expected if the samples are composed of different clay minerals and have different electrolyte contents.

CLAY MINERALS—OTHER PROPERTIES

The other properties of the clay minerals are not considered here because they are of lesser importance to a consideration of the causes of clay-material properties and the application of such information to practical problems of clay utilization. For those interested in pursuing the subject further the papers of Grim[216] and von Engle-

[212] C. S. Ross and C. W. Shannon, "Minerals of Bentonite and Related Clays and Their Properties," *Jour. Amer. Ceramic Soc.*, Vol. IX (1926), pp. 77–96; A. F. Hagner, "Adsorptive Clays of the Texas Gulf Coast," *Amer. Min.*, Vol. XXIV (1939), pp. 67–107.

[213] J. W. Gruner, "Abundance and Significance of Cristobalite in Bentonites and Fuller's Earths," *Econ. Geol.*, Vol. XXXV (1940), pp. 867–75.

[214] M. N. Bramlette and E. Posnjak, "Zeolitic Alteration of Pyroclastics," *Amer. Min.*, Vol. XVIII (1933), pp. 167–71.

[215] "Properties of Clays," *op. cit.*

[216] "Properties of Clays," *op. cit.*

hardt[217] should be consulted for optical properties; the work of Kelley and others,[218] for dehydration characteristics; the work of J. Orcel[219] and F. H. Norton,[220] for thermal analyses; the work of Grim and Bradley[221] and L. Tscheischwili and others,[222] for the changes in the clay minerals when they are fired; and the summary of W. Noll,[223] for the physical chemical conditions under which the clay minerals may be formed.

CLAY-WATER SYSTEM

The most important properties of clays are plasticity, green bonding strength, drying shrinkage, compaction, thixotropy, and viscosity of clay and water suspensions—that is, properties of clay material in the presence of water. It is obvious that a satisfactory understanding of these properties awaits precise concepts of the clay-water system. It is the object of the remainder of this report to analyze the available pertinent data and to draw from them such general concepts of clay-water structure and relationships as seem warranted. The analysis will be limited to clay-water mixtures in the plastic state.

F. Grout[224] early indicated that the most satisfactory explanation of the plastic properties of clays was based on the concept of a film of water enclosing the particles making up the clay. Many workers[225] have emphasized the importance of flake-shaped constituent

[217] *Op. cit.*

[218] "Hydration of Minerals and Soil Colloids in Relation to Crystal Structure," *Soil Sci.*, Vol. XLI (1936), pp. 259–74.

[219] "Differential Thermal Analyses in the Determination of the Constituents of Clays, Laterites, and Bauxites," *Cong. Internat. Mines, Met., geol. Appl.* 7 (1935), pp. 359–71.

[220] "Critical Study of the Differential Thermal Method for the Identification of Clay Minerals," *Jour. Amer. Ceramic Soc.*, Vol. XXII (1939), pp. 54–63.

[221] "Investigation of the Effect of Heat on the Clay Minerals Illite and Montmorillonite," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 242–48.

[222] "Metakaolin," *Ber. deutsch. keram. Gesellsch.*, Vol. XX (1939), pp. 249–76.

[223] "Mineral Formation in the System $Al_2O_3 \cdot SiO_2 \cdot H_2O$," *Neues Jahrb. f. Min.*, Vol. LXX, Abt. A (1935), pp. 65–115; "On the Conditions under which Kaolinite, Montmorillonite, Sericite, Pyrophyllite, and Analcim Can Form," *Min. u. Pet. Mitt.*, Vol. XLVIII (1936), pp. 210–46.

[224] "The Plasticity of Clay," *Trans. Amer. Ceramic Soc.*, Vol. XIV (1912), p. 71.

[225] C. Terzaghi, "The Physical Properties of Clay," *Tech. Engineer. News*, Vol. IX (1928), pp. 10, 11, 36.

particles of clays in explaining their plastic properties; and later work, particularly on the clay minerals, has substantiated both the existence of flake-shaped particles in clay materials and their importance in explaining the physical properties of these materials.

At the present time there are few students of clays who would dispute the premises that clays are composed of flake-shaped particles, that these flake-shaped particles are encased in water envelopes when the clay is in the plastic state, and that the plastic properties of clays depend to a very large degree on the characteristics of the water envelopes. By "characteristics" are meant such things as thickness, density, and orientation of the water molecules. Plasticity may be considered as a consequence of a binding force between particles tending to hold the whole mass together and a water film that separates the flakes, thereby weakening the binding force and acting as a lubricant between them. Plastic deformation is the sum total of the movement of flakes with respect to each other, the actual movement taking place in the water film.

STATE OF THE WATER IN THE ENVELOPE

Based on the work of I. Langmuir,[226] who investigated the orientation and packing of polar molecules in adsorptive films, Terzaghi[227] and others have conceived of the water envelope as being built up of layers of uniformly oriented water dipolar molecules. Slippage within the water film was postulated as occurring in the planes of the dipole ends. The idea has been held that the water of the envelope immediately adjacent to the clay-particle surface had a higher density than ordinary water, and some data in support of such increased density have been presented. On the basis of the oriented dipole concept and the increased density at the surface it was postulated that the innermost layers of dipoles were very closely packed and that the closeness of packing decreased outward.[228] R. Houwink[229] has, however, concluded that there is no increased viscosity; and W. Nitzsch[230] has presented experimental evidence

[226] "The Constitution and Fundamental Properties of Solids and Liquids," *Jour. Amer. Chem. Soc.*, Vol. XXXIX (1917), pp. 1848–1906.

[227] *Op. cit.*

[228] Grim, "Relation of Composition . . . . ," *op. cit.*

[229] *Elasticity, Plasticity, and Structure of Matter* (Cambridge: University Press, 1937).

[230] "On the Structure of the Hydration Hull of Inorganic Soil Colloids," *Kolloid Zeitschr.*, Vol. XCIII (1940), pp. 110–15.

that the first water added to dried clay materials assumes a density less than 1 and that, as more water is added, the density gradually rises to 1. According to the latter author, the swelling water of montmorillonite has a density less than 1. Recent ideas of the structure of the water film are more in accord with the findings of Houwink and Nitzsch.

Investigations of the hydrogen bond have led recently to a better understanding of the structure of the water molecule.[231] On the basis of this work Hendricks and Jefferson[232] have presented a con-

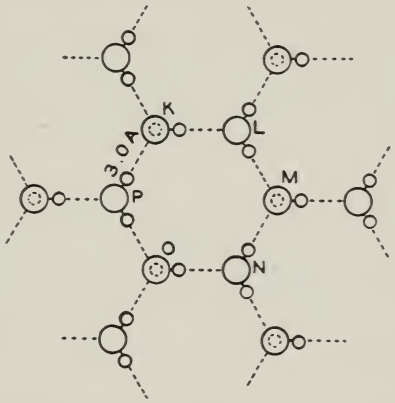

FIG. 11.—Hexagonal net of water molecules. Large spheres represent oxygen atoms and small spheres hydrogen atoms; dotted lines indicate bonding through hydrogen. (After Hendricks and Jefferson.)

cept of the structure of the water in the films. In the language of Hendricks and Jefferson a water layer is composed of water molecules joined into hexagonal groups of an extended hexagonal net as shown in projection in Figure 11. The arrangement is partly a result of a tetrahedral distribution of charge about a water molecule, two corners of the tetrahedron being occupied by hydrogen atoms and the other two corners by an excess of electrons. Each side of the hexagon (Fig. 11) must correspond to a hydroxyl bond, the hydrogen-oxygen bond of one water molecule being directed toward the

[231] J. D. Bernal and H. D. Megaw, "The Function of Hydrogen in Intermolecular Forces," *Proc. Roy. Soc. London*, Ser. A., Vol. CLI (1935), pp. 384–420. J. M. Burgers, "Introductory Remarks on Recent Investigations concerning the Structure of Liquids," *Second Rept. on Viscosity and Plasticity* (Amsterdam, 1938).

[232] *Op. cit.*

negative charge of a neighboring molecule. One-fourth of the hydrogen atoms, or a hydrogen atom of half the water molecules, are not involved in bonding within the net (*K*, *M*, and *O* of Fig. 11). Hendricks and Jefferson[233] visualize the net as being tied to the silicate sheet of the clay mineral by the attraction of those hydrogen atoms not involved in binding within the net and the oxygen atom of the neighboring silicate sheet (Fig. 12). When the surface of the clay mineral contains hydroxyl groups (e.g., kaolinite), part of the hydroxyls are free for binding through hydrogen to oxygen atoms in the water layer.

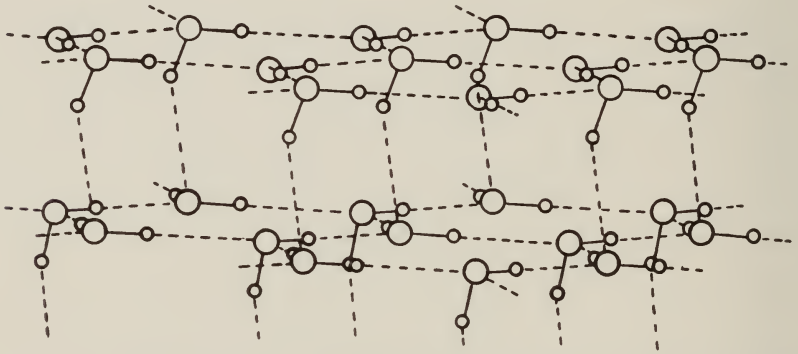

FIG. 12.—Probable structure of multiple water layers. (After Hendricks and Jefferson.)

The net has just the *a* and *b* dimensions of the silicate layer minerals if the separation of the oxygen atoms of the water molecules is about 3.0 A in projection. It is assumed that the oxygen atoms are in one plane. In this configuration there are four molecules of water for each layer in the unit structure instead of six, as in the close-packing arrangement of the older concept.[234]

The stability of the layer arises from its geometrical relationship to oxygen ions of the silicate framework (Fig. 12). Presence of the first layer favors the formation of a second, and the structure is then propagated away from the surface. The dissociation pressure of successive layers considered as hydrates would finally approach the vapor pressure of water at the temperature of observation.

[233] *Op. cit.*

[234] Bradley, Grim, and Clark, *op. cit.;* Nagelschmidt, "On the Lattice . . . . ," *op. cit.*

Kelley and his colleagues[235] have developed the concept that there are two types of adsorbed water in clays. One type, designated as "planar water," coats the plane surfaces of the flakes, is loosely held, and, as a consequence, is lost at low temperatures (−150° C.). The other type, known as "broken-bond water," is more tightly held at the edges of the sheets. Strong evidence has been presented for this concept, and it seems to fit into explanations of the plastic properties of clays.

Planar water could well have the configuration described by Hendricks and Jefferson,[236] whereas broken-bond water would be expected to have such a regular molecular orientation to a much less degree. In montmorillonite, planar water would be the dominant type; but in kaolinite and illite, broken-bond water, although not necessarily dominant, would play a more important role than in montmorillonite.

FACTORS DETERMINING THE STATE OF WATER IN THE ENVELOPE

Many investigators, but particularly Wiegner[237] and Endell, his colleague,[238] have considered that the adsorbed cations are hydrated and that a union of the solvation hulls forms the water envelope around clay-mineral particles. According to this idea, the thickness and other characteristics of the water film are a direct consequence of the hydration of the adsorbed cations that are present. This idea has become so prevalent that it has been widely accepted without critical study of the evidence for and against it.

In Table 2 values are given for the size of hydrated cations and the hydration in molecules of water per ion that have been suggested by several workers. It is obvious that there is considerable divergence in the values given by different workers and even differences in the order of hydration of the cations.[239] Attempts to measure the degree of hydration of the cations, therefore, have not provided strong evidence that the cations are actually hydrated.

J. D. Bernal and R. H. Fowler[240] some years ago presented data

[235] "Hydration of Minerals . . . . ," *op. cit.*

[236] *Op. cit.*

[237] *Op. cit.*

[238] Endell and Vageler, *op. cit.*

[239] Bar and Tenderloo, *op. cit.*

[240] "A Theory of Water in Ionic Solution with Particular Reference to Hydrogen and Hydroxyl Ions," *Jour. Chem. Phys.*, Vol. I (1933), pp. 515–48.

that threw doubt on the hydration of some cations. Bar and Tenderloo[241] have enumerated difficulties encountered by explanations of clay properties based on cation hydration, and L. D. Baver[242] has summarized experimental data on the swelling and heat of wetting of soil colloids that do not fit well with cation hydration. Hendricks and others[243] have recently presented strong evidence that

TABLE 2

ION SIZES AND IONIC HYDRATION*

	Ionic Radii in Angstroms				Hydration (Mole H_2O)				
	Not Hydrated		Hydrated						
	A	B	C	D	E	F	G	H	I
Li	0.68	0.78	10.03	7.3	12.6	10	15	11–13	13–14
Na	0.98	0.98	7.90	5.6	8.4	5	8	9–11	8–9
K	1.33	1.33	5.32	3.8	4.0	1	4	5–6	5
NH_4	.....	1.43	5.37	.....	4.4	.....	.....	2–3	.....
Rb	.....	1.49	5.09	3.6	.....	0.5	.....	.....	.....
Cs	.....	1.65	5.05	3.6	.....	0.2	.....	.....	.....
Mg	0.89	0.78	.....	10.8	13.3	33	21	20–23	.....
Ca	1.17	1.06	.....	9.6	10.0	22	22	19–22	.....
Sr	1.34	1.27	.....	9.6	8.2	21	.....	.....	.....
Ba	1.49	1.43	.....	8.8	4.1	17	14	18–20	.....
Al	0.79	0.57	.....	.....	.....	.....	57	.....	.....
La	1.30	1.22	.....	.....	.....	.....	30.5	.....	.....

* As suggested by the following authors:
A.— W. H. Zachariassen, *Zeitschr. Krist.*, Vol. LXXX (1931), p. 137.
B.— V. Goldschmidt, *Vid. Nordsk. Akad. Oslo, Skr. math.-naturv. kl.*, Vols. VII, VIII (1926, 1927).
C.— H. Jenny, *Jour. Phys. Chem.*, Vol. XXXVI (1935), pp. 2217–58.
D, F.— H. Pallman, *Bodenk Forsch.*, Vol. VI (1938), p. 21.
E.— H. Remy, *Zeitschr. Phys. Chem. Abt.*, A, Vol. XXXIX (1915), p. 467.
G.— H. Brintziner and C. Ratanarat, *Zeitschr. anorg. allgem. chem.*, Vol. CCXXII (1935), p. 119.
H.— F. Bourion, E. Ronyer, and O. Hun, *Compt. rend. Acad. sci.*, Vol. CCIV (1937), p. 1420.
I.— J. Baborovski, J. Velisch, and A. Wagner, *Jour. chim. phys.*, Vol. XXV (1928), pp. 452–82.

certain of the cations (Na^+) that were thought to be highly hydrated are probably not hydrated at all. In addition, Houwink[244] has stated that the thickness of the water film (10^2–10^3 A) is too great to be accounted for by the hydration of adsorbed cations, and Speil[245] has concluded that solvation of the adsorbed cations cannot explain fully the presence of water films. It seems, therefore, that the gen-

[241] *Op. cit.*

[242] *Soil Physics* (New York: John Wiley & Sons, 1940).

[243] *Op. cit.* [244] *Op. cit.* [245] *Op. cit.*

eral conclusion is not justified that all the common adsorbed cations are hydrated, and that some other cause for the development of the water film around the clay particles must be sought.

The lattice structures of the clay-mineral particles are continuous in the *a* and *b* crystallographic directions, so that the edges of the flakes would contain broken bonds or unsatisfied valence charges that would serve to hold water perhaps through a hydrogen bond. The explanation of the planar water is not so simple. For example, in montmorillonite, according to the structure of Hofmann and others, the basal planes are oxygens without any unsatisfied charges, and there is no obvious good reason why thick films of water should develop on them. Substitutions may occur within the lattice that develop charges on the surface, but it is believed that they are satisfied with adsorbed cations. Kelley and others[246] have suggested that planar water is due to the existence of stray forces without accounting for their source. It does not seem likely that stray forces are entirely adequate to account for the thicknesses of water films that are known to form.

According to the structure of the water sheet worked out by Hendricks and Jefferson,[247] the water is held to the clay minerals through hydroxyl bonds to oxygens or hydroxyls, and it propagates itself because of its configuration. This provides a reason for the development of a water film, but it does not explain the difference in the development of the water layers in different minerals. For example, it does not explain why montmorillonite develops such thick water sheets and pyrophyllite does not.

If one assumes that the correct structures of montmorillonite and halloysite are those suggested by Edelman and Favejee,[248] that the concept of the structure of the water layers of Hendricks and Jefferson[249] is correct, and that the oriented layers can only develop when the surface of the flakes carry projecting (OH) ions, a general concept of clay-mineral-water can be worked out that seems eminently satisfactory.

[246] "Hydration of Minerals . . . . ," *op. cit.*

[247] *Op. cit.*

[248] "On the Crystal Structure . . . . ," *op. cit.*

[249] *Op. cit.*

According to this idea, the oriented sheets of water are tied to the projecting (OH) ions of the basal sheets in montmorillonite. Montmorillonite swells because the units of the clay mineral are pushed apart by the growth of additional sheets of water (unless *certain* adsorbed cations are present that bind the sheets together, as will be discussed presently). Similarly, a water sheet develops between the layers of halloysite. In this mineral a plane of (OH) ions is adjacent to the projecting (OH) ions in the next structure unit, and this may explain why the sheet is restricted to a single layer. It must be confessed, however, that this explanation of the extra water in halloysite is no more satisfactory than those based on other concepts. Further study is necessary before the structural attributes of the halloysite minerals become well known.

Kaolinite does not develop a sheet of water between the unit cells because it does not have projecting (OH) ions.

In the case of illite, as in that of kaolinite, there are no projecting (OH) ions, and the mineral does not develop planar water between the unit cells. In natural clay materials flake-shaped particles of illite and kaolinite exist that are many unit cells thick. On the flat surfaces of these particles a water film develops. According to the suggested concept, this water would be expected to differ from water held on the flat surfaces of montmorillonite particles. For illite and kaolinite the water molecules would be oriented little or not at all, and, as a consequence, the water sheet would not develop to any considerable thickness. Stray forces that are a consequence, perhaps, of slight distortions or irregularities of the lattice may serve to hold such water.

It follows from this concept that the water envelope of a single clay mineral consists of parts held by forces of varying intensity in which the water molecules are arranged differently, and also that the amount of water molecule orientation and the binding forces vary for the different clay minerals. Thus, for kaolinite and illite there is relatively more broken-bond water than for montmorillonite. In addition, the planar water for montmorillonite differs from that of kaolinite and illite because it is made up of oriented water molecules, because it is more tightly held, and because it may extend greater distances from the flake surfaces.

INFLUENCE OF ADSORBED CATIONS ON THE WATER FILM

It has been pointed out that it is highly questionable whether some of the cations previously thought to be highly hydrated actually are hydrated at all. It is equally questionable whether other cations hydrate to the degree that has been postulated. There remain to be analyzed other ways in which adsorbed cations may affect the water film.

Jenny[250] and, later, J. D. Sullivan[251] have pointed out that ions of large volume would occupy more space than ions of lesser volume and, consequently, that when large ions are present there would be less space available for water molecules. Thus, 1 Ca^{++} of volume 4.99 A^3 will replace 2 Na^+ with a combined volume of 7.88 A^3. However, in view of the facts that the cations are smaller than the water molecules and that the water molecules are packed loosely, it appears unlikely that a clogging effect is important.

It has long been believed that adsorbed cations exert a polarizing effect on the water of the film. According to Jenny,[252] the polarizing effect is stronger the greater the charge and the smaller the radius. Burgers[253] has suggested that adsorbed cations exert a tightening effect on the configuration of the water sheet. Perhaps this is not at variance with the polarizing effect, although it must be admitted that the precise effect of cations on the configuration of the water molecules is not clear.

Data from investigations of the relation of exchangeable bases to plastic properties indicate that in some way the character of the adsorbed cation affects the thickness of the water film. In the absence of hydration of the cations it seems likely that the effect is produced by a binding action of the cations. That is to say that cations act as bridges to bind the clay-mineral sheets together. The action is analogous to the effect of K^+ in holding together the unit cells of muscovite in the direction of the *c*-axis. This idea does not preclude a slight hydration of certain ions, but it postulates the

[250] "Cation and Anion Exchanges on the Interface of Permutite," *Kolloidchem.*, Vol. XXIII (1927), pp. 428–72.

[251] "Physico-chemical Control of Properties of Clay," *Trans. Electrochem. Soc.*, Vol. LXXV (1939), pp. 71–97.

[252] "Studies on the Mechanism . . . . " *op. cit.* [253] *Op. cit.*

adsorbed cations as controlling the thickness of the film water primarily by means of the force with which they hold the sheets together.

In applying this idea to montmorillonite it follows that the thickness of the water film is the result of two opposing forces: (*a*) the tendency of layers of water to develop on the basal planes, for reasons already discussed; and (*b*) the tendency of the adsorbed cations to hold the sheets together. The resulting thickness of the film is chiefly dependent on the cation. The bonding action of the adsorbed cations is not a new concept, but its significance has perhaps not been appreciated fully.

It may be postulated that the bridging action of the adsorbed cations varies with their valence and perhaps also with their size. With regard to the latter factor, the work of Page[254] suggests that, for ions of equal valence, those with a diameter about equal to that of the hole in the hexagonal net of the silica sheet would exert the greatest bonding action.

It is a well-known fact that Na-montmorillonite expands greatly in the presence of abundant water, whereas under similar conditions Ca-montmorillonite expands very little. According to this concept, the great swelling of the Na-montmorillonite is due not to the hydration of the Na^+ serving as a wedge to force the layers apart but to the absence of a strong bridge because of the univalent character of Na^+ and perhaps also because of its small size enabling it to fit well in the hole of the silica sheet. The Ca-montmorillonite does not expand greatly because of the slight hydration of Ca^{++} but because the divalent ion holds the layers together so that a thick series of water sheets cannot form between them.

It is also a well-known fact that completely electrodialyzed montmorillonite expands only very slightly. On the basis of the above concept, it would seem at first that the H-montmorillonite should swell more avidly than Na-montmorillonite. That, perhaps, would be true if H-montmorillonite contained only H^+ as the adsorbed cation. There is a considerable body of data to indicate that, before all the adsorbed cations are replaced by H^+, some Al^{+++} is removed

[254] *Op. cit.*

from the lattice to occupy exchange positions. Many workers[255] have presented experimental evidence for this point. An explanation for the nonswelling of so-called "H-montmorillonite clays" is that they are not pure H-montmorillonites but also contain multivalent cations that serve to bind the layers together.

What has been said has been developed with particular reference to montmorillonite clay materials. It can also be applied to clay materials composed of other clay minerals. In illites and kaolinites the water does not penetrate between the basal planes of the unit cells. The planar water occurs on aggregates and, as pointed out before, is probably held by weaker forces than those operating in montmorillonite. Likewise, illite and kaolinite have low capacity for holding adsorbed cations, so that the forces holding the clay-mineral aggregates to each other would be less than in montmorillonite clay materials. It may be concluded that the total area encased by water in illite and kaolinite clay materials would be less than in those composed of montmorillonite. It can also be concluded that a smaller part of the total water of illite and kaolinite clay materials would show a definite configuration than of montmorillonite clay materials and that the configuration would be less regular in the former types of materials than in the latter types.

PLASTIC PROPERTIES OF CLAY MATERIALS ON THE BASIS OF THE FOREGOING CONCEPT

Clays composed of illite and kaolinite clay minerals tend to adsorb less water, to have lower green bonding strength, as expressed in terms of modulus of rupture of the clay alone or when determined for sand-clay mixtures, to be more permeable to water, and to shrink less and more rapidly than clays composed of montmorillonite.[256] These differences in properties would be expected on the basis of the concept outlined.

Sullivan and Graham,[257] G. J. Barker and E. Truog,[258] and Speil[259]

[255] Hendricks and Alexander, *op. cit.;* Hofmann and Giese, *op. cit.;* G. Volk, "Nature of Potash Fixation in Soils," *Soil Sci.*, Vol. XLV (1938), pp. 263–76.

[256] Grim, "Relation of Composition . . . . ," *op. cit.* [257] *Op. cit.*

[258] "Improvement of Stiff Mud Clays through pH Control," *Jour. Amer. Ceramic Soc.*, Vol. XXI (1938), pp. 324–29.

[259] *Op. cit.*

have shown that clays carrying Na^+ require less tempering water than H^+ clays to attain the same degree of stiffness or the same yield-point when force is applied to the plastic mass. Stated another way, if clays of the same water content are compared, the Na-clay will be less stiff and will yield with lower applied pressure than the H-clay. The order of increasing yield-point (ability to hold shape) with a given water content is approximately as follows:[260] Li^+, Na^+, Ca^{++}, Ba^{++}, Mg^{++}, Al^{+++}, K^+, Fe^{+++}, NH_4^+, H^+. In this series there is considerable difference between the effect of Li^+ and Na^+ and that of Ca^{++}. The difference between the other members of the series is not very great. This series is in agreement with expected results if it is considered that the so-called "H-clays" carry Al^{+++}. The position of Li^+ and Na^+ would be a consequence of their low power to bind the clay-mineral flakes together. Little water would therefore be required between the sheets for the mass to yield; or, if much water were present, the mass would yield with low applied pressure.

Na-clays are reported[261] to show very high Atterberg Plastic Indices that result from very low Lower Plastic Limits and very high Lower Liquid Limits. From what has just been said, the value for the Lower Plastic Limit would be expected. Also, the high value for Lower Liquid Limit would be expected in the absence of multivalent cations binding the clay mineral particles together and impeding the full development of the water envelope.

Extensive data regarding the effect of exchangeable cations on bonding strength are not yet at hand. Available data suggest that the strength in the green (i.e., moist) condition is greater for Ca- and H-clays than for Na-clays and that the reverse relationship is true for strength in the dried[262] but unfired condition. The green-strength relationship is clear on the basis of the low bonding power of Na^+, but the explanation for the dry-strength relationship is not

[260] J. D. Sullivan and R. P. Graham, "Effect of Exchangeable Bases on Torsion Properties of Clay," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 39–51.

[261] Endell, Fendius, and Hofmann, *op. cit.*

[262] Speil, *op. cit.;* Graham and Sullivan, "Effect of Base-Exchange on Absorption and Transverse Strength of Clay Bodies," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 52–56.

entirely clear, unless it is considered that dry strength is a function of the total available surface area of the clay-mineral particles. With the low bonding power of the particles for each other in the Na-clay the tendency would be for the component clay-mineral particles to disaggregate and form a huge surface area per volume of clay.

It is well known[263] that Na-clays dry more slowly than Ca- or H-clays. An explanation is that the water in the Na-clay penetrates more completely between sheets; or, stated another way, the clay-mineral units separated by the water are smaller and the water itself occurs in smaller spaces. A further factor that may be of importance is that in Na-clays there is little binding force between the clay-mineral flakes to speed up drying by squeezing action on the water.

Speil[264] has shown that substitution of Na^+ for H^+ on a kaolinite clay tends to decrease both the pore water and shrinkage water. The suggested explanation, in addition to that already given, is that particles with low attractive forces between them (Na-clay) could come into a more compact arrangement, whereas particles with high attractive forces between them would be pulled together into a random arrangement before they reached the most compact positions. The random arrangement would be expected to give a relatively higher pore-water value.

Na-montmorillonite adsorbs water and is much less permeable than Ca-montmorillonite. The high water adsorption of Na-montmorillonite is expected because the flakes are held together loosely, so that a large amount of water can enter between them. The low permeability is in accordance with the discussion of rate of drying.

It would seem, therefore, that the suggested concept agrees with certain important plastic properties of clays. Whether it is successful in explaining all or even most of the plastic properties of clays remains to be determined by future work.

[263] Sullivan and Graham, "Effect of Exchangeable Bases on the Drying of Clay Bodies," *Jour. Amer. Ceramic Soc.*, Vol. XXIII (1940), pp. 57–61; C. G. Harman, "Physical and Chemical Characteristics of Clay Related to Their Working Properties," *Brick and Clay Rec.*, Vol. XCIV (1939), pp. 26–27.

[264] *Op. cit.*